

The “conservative” property

A thermodynamic variable C is said to be “conservative” if its evolution equation (that is, its prognostic equation) has the form

$$(\rho C)_t + \nabla \cdot (\rho \mathbf{u} C) = \rho \frac{dC}{dt} = -\nabla \cdot \mathbf{F}^C. \quad (\text{A.8.1})$$

For such a “conservative” property, in the absence of fluxes \mathbf{F}^C at the boundary of a control volume, the total amount of C -stuff is constant inside the control volume. In the special case when the material derivative of a property is zero (that is, the middle part and the right-hand side of Eqn. (A.8.1) are zero) the property is said to be “materially conserved”.

The only three quantities that can be regarded as 100% conservative in the ocean are (1) mass [equivalent to taking $C = 1$ and $\mathbf{F}^C = \mathbf{0}$ in Eqn. (A.8.1), giving the continuity equation, which is the equation representing the conservation of mass], (2) total energy $\mathcal{E} = u + \frac{1}{2} \mathbf{u} \cdot \mathbf{u} + \Phi$ (see Eqn. (B.15)), and (3) Preformed Salinity S_* . Conservative Temperature Θ (or equivalently, potential enthalpy h^0) is not completely conservative, but we will find that the error in assuming it to be conservative is negligible. Because we are ignoring the non-conservative source term of Absolute Salinity in this course, we may also take Absolute Salinity to be conservative (as we have done in going from Eqn. (B.20) to Eqn. (B.20a) above).

Other variables such as potential temperature θ , enthalpy h , internal energy u , entropy η , density ρ , potential density ρ^\ominus , specific volume v , potential specific volume, v^\ominus , and the Bernoulli function $\mathcal{B} = h + \frac{1}{2} \mathbf{u} \cdot \mathbf{u} + \Phi$ (see Eqn. (B.17)) are not conservative variables.

The “isobaric conservative” property

A different form of “conservation” attribute, namely “isobaric conservation” occurs when the total amount of the quantity is conserved when two fluid parcels are mixed at constant pressure without external input of heat or matter. This “isobaric conservative” property is a very valuable attribute for an oceanographic variable. Any “conservative” variable is also “isobaric conservative”, thus the conservative variables listed above, namely mass, total energy \mathcal{E} and Preformed Salinity S_* are exactly “isobaric conservative” variables, while Absolute Salinity S_A is almost (but not exactly) “isobaric conservative”.

In addition, the Bernoulli function \mathcal{B} and specific enthalpy h are also almost exactly “isobaric conservative”. The issue with the Bernoulli function in this regard is the presence of the unsteady term P_t , while the issue with enthalpy not being totally 100% “isobaric conservative” is the presence of the dissipation of mechanical energy $\rho \epsilon$. We will find that this is also the largest of several terms that cause Conservative Temperature and specific potential enthalpy h^0 to not be 100% “conservative” or “isobaric conservative”. Note that while h is almost exactly “isobaric conservative”, it is not a “conservative” variable.

Some variables that are not “isobaric conservative” include potential temperature θ , internal energy u , entropy η , density ρ , potential density ρ^\ominus , specific volume v , and potential specific volume v^\ominus .

The “potential” property

Any thermodynamic property of seawater that remains constant when a parcel of seawater is moved from one pressure to another adiabatically, without exchange of mass and without interior conversion between its turbulent kinetic and internal energies, is said to possess the “potential” property, or in other words, to be a “potential” variable. Prime examples of “potential” variables are entropy η , potential temperature θ and potential density ρ^\ominus . Recall that the constancy of entropy η can be seen from the First Law of Thermodynamics in Eqn. (B.19);

$$\boxed{\rho \left(\frac{dh}{dt} - v \frac{dP}{dt} \right) = \rho \left(\frac{du}{dt} + (p + P_0) \frac{dv}{dt} \right) = \rho \left((T_0 + t) \frac{d\eta}{dt} + \mu \frac{dS_A}{dt} \right)} \quad (\text{B.19})$$

$$= -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \epsilon$$

since, with the right-hand side of Eqn. (B.19) being zero, and with no change in Absolute Salinity, it follows that entropy is also constant. Any thermodynamic property that is a function of only Absolute Salinity and entropy also remains unchanged by this procedure and is said to possess the “potential” property.

Recall that in oceanography we now define the word “adiabatic” to describe a process occurring without exchange of heat and also without the internal dissipation of kinetic energy. With this definition of “adiabatic”, a process that is both isohaline and adiabatic *does* imply that the entropy η , potential temperature θ and Conservative Temperature Θ are all constant.

Thermodynamic properties that possess the “potential” attribute include potential temperature θ , potential enthalpy h^0 , Conservative Temperature Θ , potential density ρ^\ominus and potential specific volume v^\ominus (no matter what fixed reference pressure is chosen). Some thermodynamic properties that do not possess the potential property are temperature t , enthalpy h , internal energy u , specific volume v , density ρ , specific volume v , specific volume anomaly δ , total energy \mathcal{E} and the Bernoulli function \mathcal{B} . From Eqn. (B.17) we notice that in the absence of molecular fluxes the Bernoulli function \mathcal{B} is constant following the fluid flow only if the pressure field is steady; in general this is not the case. The non-potential nature of \mathcal{E} is explained in the discussion following Eqn. (B.17) on page 22 of these lecture notes.

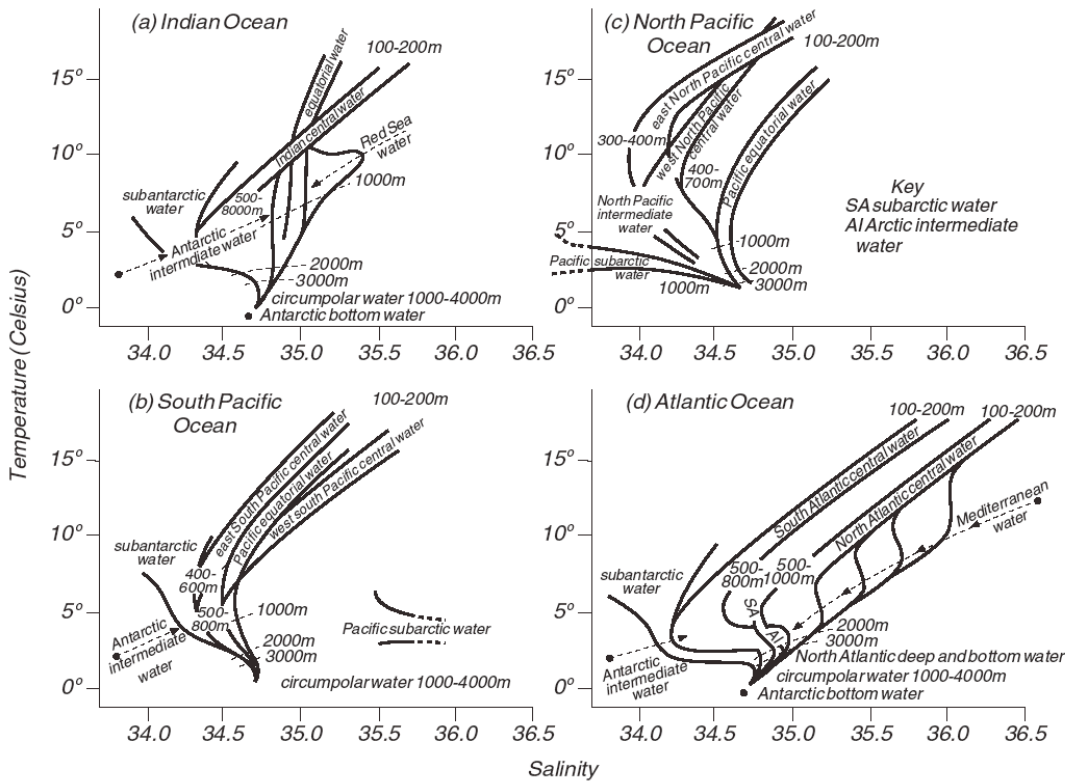


Figure 13.11 T - S plots of water in the various ocean basins. After Tolmazin (1985: 138).

Oceanographers analyze “water-masses” on this $S_A - \Theta$ diagram. The salinity and temperature variables on these axes should ideally be both “potential” and “conservative” properties so that turbulent mixing processes can be accurately visualized on such a diagram.

A “water mass” is defined to be a line (not necessarily a straight line) on this $S_A - \Theta$ diagram.

The figure below is of near-surface water from the global ocean. It is a bit of a mess, with some regions being plotted on top of others, but some are distinct.

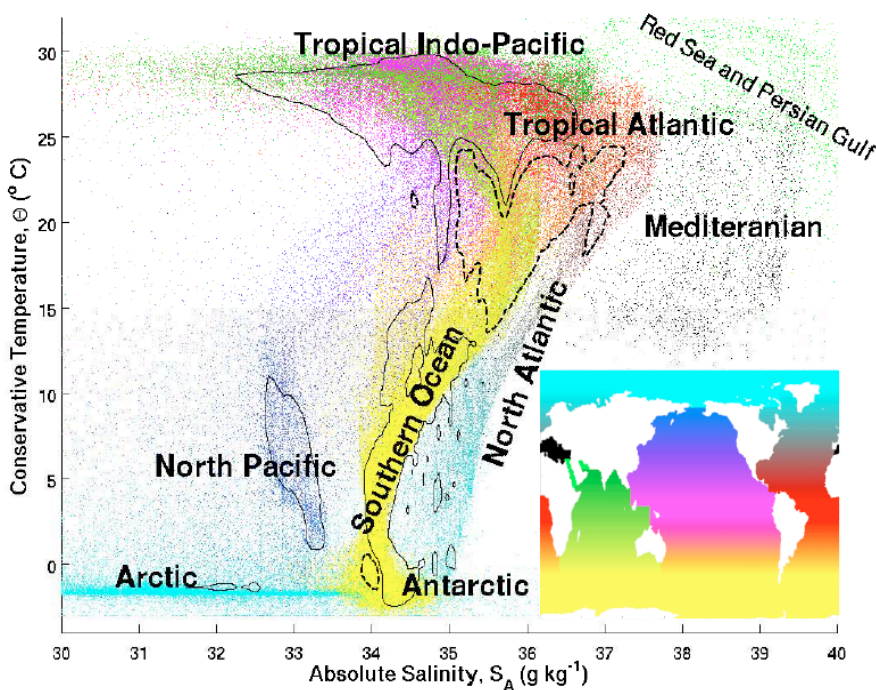


Table A.9.1 The “potential”, “conservative”, “isobaric conservative” and the functional nature, of various oceanographic variables

Variable	“potential”?	“conservative”?	“isobaric conservative”?	function of (S_A, t, p) ?
S_*	✓	✓	✓	✗
S_A	✓	✗ ¹	✗ ¹	✓
t	✗	✗	✗	✓
θ	✓	✗	✗	✓
η	✓	✗	✗	✓
h	✗	✗	✓ ²	✓
Θ, h^0	✓	✓ ³	✓ ³	✓
u	✗	✗	✗	✓
\mathcal{B}	✗	✗	✓ ⁴	✗
\mathcal{E}	✗	✓ ⁴	✓ ⁴	✗
ρ, ν	✗	✗	✗	✓
ρ^\ominus	✓	✗	✗	✓
δ	✗	✗	✗	✓
γ^n	✗	✗	✗	✗

¹ The remineralization of organic matter changes S_A .

² Taking ε and the effects of remineralization to be negligible.

³ Taking ε and other terms of similar size to be negligible (see the discussion following Eqn. (A.21.13)).

⁴ Taking the effects of remineralization to be negligible.

In Table A.9.1 various oceanographic variables are categorized according to whether they possess the “potential” property, whether they are “conservative” variables, whether they are “isobaric conservative”, and whether they are functions of only (S_A, t, p) . Note that Θ is the only variable that achieves four “ticks” in this table, while Preformed Salinity S_* has ticks in the first three columns, but not in the last column since it is a function not only of (S_A, t, p) (since it also depends on the composition of seawater). Hence Θ is the most “ideal” thermodynamic variable. If it were not for the non-conservation of Absolute Salinity, it too would be an “ideal” thermodynamic variable, but in this sense, Preformed Salinity is superior to Absolute Salinity. Conservative Temperature Θ and Preformed Salinity S_* are the only two variables in this table to be both “potential” and “conservative”. The last three rows of Table A.9.1 are for potential density, ρ^\ominus , specific volume anomaly, δ , and Neutral Density γ^n . We will discuss these variables later in the course.

In this course we are assuming that Absolute Salinity is 100% conservative (hence the **yellow highlighting** in the table above). This is not strictly true. The important thing is that we use Absolute Salinity and not Practical or Reference Salinity in an ocean model and as the salinity argument to the expression for density. The non-conservative source term of Absolute Salinity is small on a timescale of less than a century.

Proof that $\theta = \theta(S_A, \eta)$ and $\Theta = \Theta(S_A, \theta)$

Consider changes occurring at the sea surface, (specifically at $p = 0$ dbar) where the temperature is the same as the potential temperature referenced to 0 dbar and the increment of pressure dp is zero. Regarding specific enthalpy h and chemical potential μ to be functions of entropy η (in place of temperature t), that is, considering the functional form of h and μ to be $h = \hat{h}(S_A, \eta, p)$ and $\mu = \hat{\mu}(S_A, \eta, p)$, it follows from the Fundamental Thermodynamic Relation (Eqn. (A.7.1)) that

$$\hat{h}_\eta(S_A, \eta, 0) d\eta + \hat{h}_{S_A}(S_A, \eta, 0) dS_A = (T_0 + \theta) d\eta + \hat{\mu}(S_A, \eta, 0) dS_A, \quad (\text{A.10.1})$$

which shows that specific entropy η is simply a function of Absolute Salinity S_A and potential temperature θ , that is $\eta = \tilde{\eta}(S_A, \theta)$, with no separate dependence on pressure. It follows that $\theta = \theta(S_A, \eta)$.

Similarly, from the definition of potential enthalpy and Conservative Temperature in Eqns. (3.2.1) and (3.3.1), at $p = 0$ dbar it can be seen that the Fundamental Thermodynamic Relation (A.7.1) implies

$$dh^0 = c_p^0 d\Theta = (T_0 + \theta) d\eta + \tilde{\mu}(S_A, \theta, 0) dS_A. \quad (\text{A.10.2})$$

This shows that Conservative Temperature is also simply a function of Absolute Salinity and potential temperature, $\Theta = \tilde{\Theta}(S_A, \theta)$, with no separate dependence on pressure. It then follows that Θ may also be expressed as a function of only S_A and η . It follows that Θ has the “potential” property.

So we see that the four variables S_A , θ , η and Θ are all “potential” variables, they are all properties of a seawater parcel, they are all independent of pressure (for adiabatic and isohaline pressure changes), and they are related to each other in the sense that if you know any two of them, you know the other two. Absolute Salinity S_A has a clear meaning and is different in character to the other three variables θ , η and Θ which are very “temperature-like” variables.

Various isobaric derivatives of specific enthalpy

We will not derive the following derivatives here, but here they are.

$$\left. \frac{\partial \hat{h}}{\partial \eta} \right|_{S_A, p} = (T_0 + t) \quad (\text{A.11.5a})$$

$$\left. \frac{\partial \hat{h}}{\partial S_A} \right|_{\eta, p} = \mu. \quad (\text{A.11.5b})$$

$$\boxed{\left. \tilde{h}_\theta \right|_{S_A, p} = c_p(S_A, \theta, 0) \frac{(T_0 + t)}{(T_0 + \theta)} = -(T_0 + t) g_{TT}(S_A, \theta, 0).} \quad (\text{A.11.9})$$

$$\boxed{\begin{aligned} \left. \tilde{h}_{S_A} \right|_{\theta, p} &= \mu(S_A, t, p) - (T_0 + t) \mu_T(S_A, \theta, 0) \\ &= g_{S_A}(S_A, t, p) - (T_0 + t) g_{TS_A}(S_A, \theta, 0). \end{aligned}} \quad (\text{A.11.11})$$

$$\boxed{\left. \hat{h}_\Theta \right|_{S_A, p} = \frac{(T_0 + t)}{(T_0 + \theta)} c_p^0.} \quad (\text{A.11.15})$$

$$\boxed{\begin{aligned} \left. \hat{h}_{S_A} \right|_{\Theta, p} &= \mu(S_A, t, p) - \frac{(T_0 + t)}{(T_0 + \theta)} \mu(S_A, \theta, 0) \\ &= g_{S_A}(S_A, t, p) - \frac{(T_0 + t)}{(T_0 + \theta)} g_{S_A}(S_A, \theta, 0). \end{aligned}} \quad (\text{A.11.18})$$

Differential relationships between η , θ , Θ and S_A

Taking specific enthalpy to be a function of potential temperature (rather than of temperature t), that is, taking $h = \tilde{h}(S_A, \theta, p)$, the fundamental thermodynamic relation (A.7.1) becomes

$$\tilde{h}_\theta d\theta + \tilde{h}_{S_A} dS_A = (T_0 + t)d\eta + \mu dS_A \quad \text{while} \quad \partial\tilde{h}/\partial P|_{S_A, \theta} = v. \quad (\text{A.11.6})$$

Similarly, considering specific enthalpy to be a function of Conservative Temperature (rather than of temperature t), that is, taking $h = \hat{h}(S_A, \Theta, p)$, the fundamental thermodynamic relation (A.7.1) becomes

$$\hat{h}_\Theta d\Theta + \hat{h}_{S_A} dS_A = (T_0 + t)d\eta + \mu dS_A \quad \text{while} \quad \partial\hat{h}/\partial P|_{S_A, \Theta} = v. \quad (\text{A.11.12})$$

Using these forms of the Fundamental Thermodynamic Relation, together with the four boxed equations for the partial derivative of enthalpy (A.11.9), (A.11.11), (A.11.15) and (A.11.18), we find

$$\begin{aligned} (T_0 + t)d\eta + \mu(p)dS_A &= \frac{(T_0 + t)}{(T_0 + \theta)} c_p(0) d\theta + \left[\mu(p) - (T_0 + t)\mu_T(0) \right] dS_A \\ &= \frac{(T_0 + t)}{(T_0 + \theta)} c_p^0 d\Theta + \left[\mu(p) - \frac{(T_0 + t)}{(T_0 + \theta)} \mu(0) \right] dS_A. \end{aligned} \quad (\text{A.12.1})$$

The quantity $\mu(p)dS_A$ is now subtracted from each of these three expressions and the whole equation is then multiplied by $(T_0 + \theta)/(T_0 + t)$ obtaining

$$(T_0 + \theta)d\eta = c_p(0) d\theta - (T_0 + \theta)\mu_T(0) dS_A = c_p^0 d\Theta - \mu(0) dS_A. \quad (\text{A.12.2})$$

From this follows all the following partial derivatives between η , θ , Θ and S_A ,

$$\Theta_\theta|_{S_A} = c_p(S_A, \theta, 0)/c_p^0, \quad \Theta_{S_A}|_\theta = [\mu(S_A, \theta, 0) - (T_0 + \theta)\mu_T(S_A, \theta, 0)]/c_p^0, \quad (\text{A.12.3})$$

$$\Theta_\eta|_{S_A} = (T_0 + \theta)/c_p^0, \quad \Theta_{S_A}|_\eta = \mu(S_A, \theta, 0)/c_p^0, \quad (\text{A.12.4})$$

$$\theta_\eta|_{S_A} = (T_0 + \theta)/c_p(S_A, \theta, 0), \quad \theta_{S_A}|_\eta = (T_0 + \theta)\mu_T(S_A, \theta, 0)/c_p(S_A, \theta, 0), \quad (\text{A.12.5})$$

$$\theta_\Theta|_{S_A} = c_p^0/c_p(S_A, \theta, 0), \quad \theta_{S_A}|_\Theta = -[\mu(S_A, \theta, 0) - (T_0 + \theta)\mu_T(S_A, \theta, 0)]/c_p(S_A, \theta, 0), \quad (\text{A.12.6})$$

$$\eta_\theta|_{S_A} = c_p(S_A, \theta, 0)/(T_0 + \theta), \quad \eta_{S_A}|_\theta = -\mu_T(S_A, \theta, 0), \quad (\text{A.12.7})$$

$$\eta_\Theta|_{S_A} = c_p^0/(T_0 + \theta), \quad \eta_{S_A}|_\Theta = -\mu(S_A, \theta, 0)/(T_0 + \theta). \quad (\text{A.12.8})$$

The First Law of Thermodynamics in terms of θ , η and Θ

Here we repeat the First Law of Thermodynamics

$$\rho \left(\frac{dh}{dt} - v \frac{dP}{dt} \right) = \rho \left(\frac{du}{dt} + (p + P_0) \frac{dv}{dt} \right) = \rho \left((T_0 + t) \frac{d\eta}{dt} + \mu \frac{dS_A}{dt} \right) = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon \quad (\text{B.19})$$

We wish to interpret this statement as a conservation statement for a “potential” variable, since this is how ocean models treat their heat-like variable, which to date has been potential temperature θ . None of enthalpy h , internal energy u or specific volume v are “potential” variables. Rather, these variables change simply due to a change in pressure even in the absence of heat or salt fluxes. The “heat-like” variables that are “potential” variables are entropy η , potential temperature θ , and Conservative Temperature Θ .

The First Law of Thermodynamics, Eqn. (B.19), can be written as an evolution equation for entropy as

$$\rho \left((T_0 + t) \frac{d\eta}{dt} + \mu \frac{dS_A}{dt} \right) = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon \quad (\text{A.13.3})$$

The First Law of Thermodynamics can also be written in terms of potential temperature θ (with respect to reference pressure $p_r = 0$) by taking $h = \hat{h}(S_A, \theta, p)$ and using Eqns. (A.11.9) and (A.11.11) as

$$\rho \left(\frac{(T_0 + t)}{(T_0 + \theta)} c_p(0) \frac{d\theta}{dt} + \left[\mu(p) - (T_0 + t) \mu_T(0) \right] \frac{dS_A}{dt} \right) = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon \quad (\text{A.13.4})$$

while in terms of Conservative Temperature Θ , the First Law of Thermodynamics is (using $h = \hat{h}(S_A, \Theta, p)$ and Eqns. (A.11.15) and (A.11.18))

$$\rho \left(\frac{(T_0 + t)}{(T_0 + \theta)} c_p^0 \frac{d\Theta}{dt} + \left[\mu(p) - \frac{(T_0 + t)}{(T_0 + \theta)} \mu(0) \right] \frac{dS_A}{dt} \right) = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon \quad (\text{A.13.5})$$

A quick ranking of these three variables, η , θ and Θ , from the viewpoint of the amount of their non-conservation, can be gleaned by examining the range of the red terms (at fixed pressure) that multiply the material derivatives on the left-hand sides of the above Eqns. (A.13.3), (A.13.4) and (A.13.5).

Why are we able to settle for examining the variation of these red terms only at constant pressure? The ocean circulation may be viewed as a series of adiabatic and isohaline movements of seawater parcels interrupted by a series of isolated turbulent mixing events. During any of the adiabatic and isohaline transport stages every “potential” property is constant, so each of the above variables, entropy, potential temperature and Conservative Temperature are 100% ideal during these adiabatic and isohaline advection stages. The turbulent mixing events occur at fixed pressure so the non-conservative production of say entropy depends on the extent to which the coefficients $(T_0 + t)$ and μ in Eqn. (A.13.3) vary at fixed pressure.

Similarly the non-conservative production of potential temperature depends on the extent to which the coefficients $c_p(0)(T_0 + t)/(T_0 + \theta)$ and $[\mu(p) - (T_0 + t)\mu_T(0)]$ in Eqn. (A.13.4) vary at fixed pressure, while the non-conservative production of Conservative Temperature depends on the extent to which the coefficients $(T_0 + t)/(T_0 + \theta)$ and $[\mu(p) - \mu(0)(T_0 + t)/(T_0 + \theta)]$ in Eqn. (A.13.5) vary at fixed pressure.

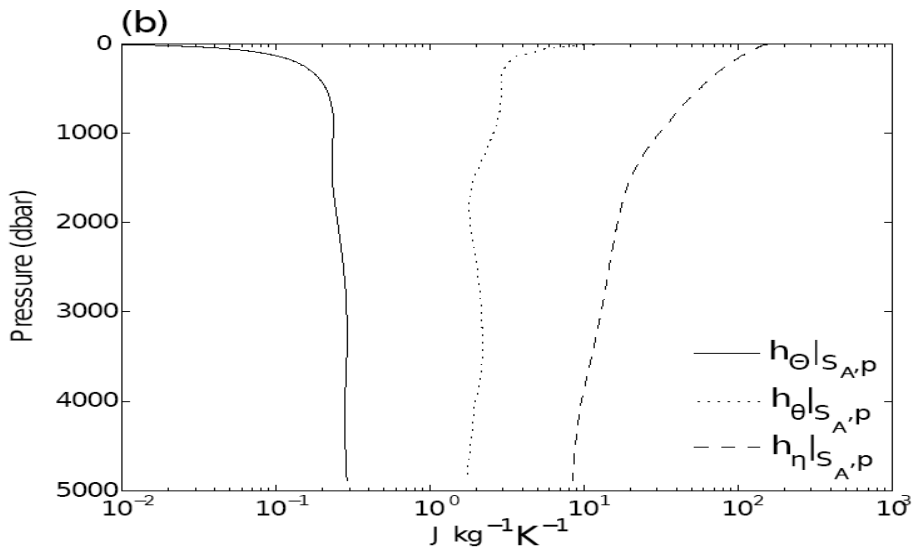
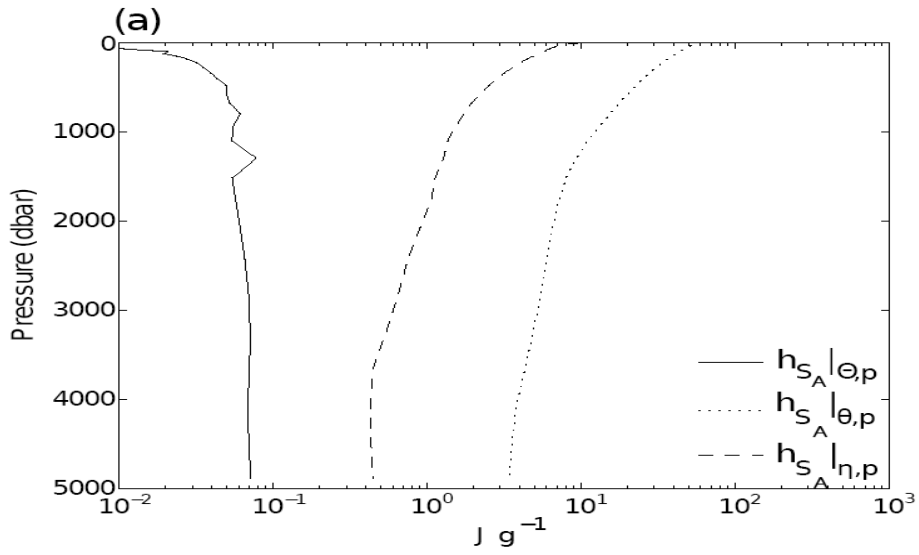
According to this way of looking at these equations we note that the material derivative of entropy appears in Eqn. (A.13.3) multiplied by the

absolute temperature (T_0+t) which varies by about 15% at the sea surface $((273.15+40)/273.15 \approx 1.146)$, the term that multiplies $d\theta/dt$ in (A.13.4) is dominated by the variations in the isobaric specific heat $c_p(S_A, t, p_t)$ which is mainly a function of S_A and which varies by 5.5% at the sea surface (see **Figure 4** on page 1), while the material derivative of Conservative Temperature $d\Theta/dt$ in Eqn. (A.13.5) is multiplied by the product of a constant “heat capacity” c_p^0 and the factor $(T_0+t)/(T_0+\theta)$ which varies very little in the ocean, especially when one realizes that it is only the variation of this ratio at each pressure level that is of concern. This factor is unity at the sea surface and is also very close to unity in the deep ocean.

More quantitatively, the r.m.s. variation of these six terms is shown in the following figure (from Graham, F. S. and T. J. McDougall, 2013: Quantifying the non-conservative production of Conservative Temperature, potential temperature and entropy. *Journal of Physical Oceanography*, **43**, 838-862.). The variations of temperature in the ocean are about five times as large as the variations of Absolute Salinity (in g/kg) so if the horizontal axis of Fig (a) is divided by a factor of 5, the figures can be compared numerically.

This figure shows that both the red terms in the potential temperature version of the First Law contribute to non-conservation about equally (we will find out why shortly). The non-constancy of the terms that multiply dS_A/dt in both the entropy and Conservative Temperature cases are very small compared to the variation of the terms multiplying $d\eta/dt$ and $d\Theta/dt$ respectively.

So the ranking of the variables can be seen simply by looking at Fig (b), especially if we mentally move the dotted line (the line for θ) to the right by a factor of two.



Review of the last lecture

We discussed potential temperature, both for a real liquid (like seawater) and for a perfect gas, where things are considerably simpler.

We then extended the “potential” concept to enthalpy, defining potential enthalpy, and writing down the relationship between enthalpy and potential enthalpy as a pressure integral of specific volume.

The “conservative” and “isobaric conservative” properties were defined, and many oceanographic variables were categorized according to whether they are “potential” variables, “conservative” variables, “isobaric conservative” variables, and according to whether they are thermodynamic variables (that is, variables that are a function of Absolute Salinity, temperature and pressure).

We proved that once you know the Absolute Salinity of a seawater parcel as well as one of entropy, potential temperature or Conservative Temperature, then you know the other two of these “temperature-like” variables.

We used the various partial derivatives of enthalpy to rewrite the First Law of Thermodynamics

$$\rho \left(\frac{dh}{dt} - v \frac{dP}{dt} \right) = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon , \quad (\text{B.19})$$

as

$$\rho \left((T_0 + t) \frac{d\eta}{dt} + \mu \frac{dS_A}{dt} \right) = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon , \quad (\text{A.13.3})$$

$$\rho \left(\frac{(T_0 + t)}{(T_0 + \theta)} c_p(0) \frac{d\theta}{dt} + \left[\mu(p) - (T_0 + t) \mu_T(0) \right] \frac{dS_A}{dt} \right) = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon , \quad (\text{A.13.4})$$

$$\rho \left(\frac{(T_0 + t)}{(T_0 + \theta)} c_p^0 \frac{d\Theta}{dt} + \left[\mu(p) - \frac{(T_0 + t)}{(T_0 + \theta)} \mu(0) \right] \frac{dS_A}{dt} \right) = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon . \quad (\text{A.13.5})$$

We then estimated a rough ranking of entropy, potential temperature and Conservative Temperature, in terms of how “conservative” these variables are. We did this by simply seeing how much the partial derivative of enthalpy with respect to these variables varied at fixed pressure in the ocean.

Non-conservative production of entropy

Here the non-conservative nature of entropy will be quantified by considering the mixing of a pair of seawater parcels at fixed pressure. The mixing is taken to be complete so that the end state is a seawater parcel that is homogeneous in Absolute Salinity and entropy. That is, we will be considering mixing to completion by a turbulent mixing process.

Consider the mixing of two fluid parcels (parcels 1 and 2) that have initially different temperatures and salinities. The mixing process occurs at pressure p . Because the mixing is assumed to happen to completion, it follows that in the final state Absolute Salinity, entropy and all the other properties are uniform. Assuming that the mixing happens with a vanishingly small amount of dissipation of kinetic energy, the ε term can be dropped from the First Law of Thermodynamics, (A.13.1), this equation becoming

$$(\rho h)_t + \nabla \cdot (\rho \mathbf{u} h) = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q. \quad \text{at constant pressure (A.16.1)}$$

Note that this equation has the “conservative” form and so h is conserved during mixing at constant pressure, that is, h is “isobaric conservative”. In the case we are considering of mixing the two seawater parcels, the system is closed and there are no radiative, boundary or molecular heat fluxes coming through the outside boundary so the integral over space and time of the right-hand side of Eqn. (A.16.1) is zero. The surface integral of $(\rho \mathbf{u} h)$ through the boundary is also zero because there is no flow through the boundary. Hence it is apparent that the volume integral of ρh is the same at the final state as it is at the initial state, that is, enthalpy is conserved. Hence during the mixing process the mass, salt content and enthalpy are conserved, that is

$$m_1 + m_2 = m, \quad (\text{A.16.2})$$

$$m_1 S_{A1} + m_2 S_{A2} = m S_A, \quad (\text{A.16.3})$$

$$m_1 h_1 + m_2 h_2 = m h, \quad (\text{A.16.4})$$

while the non-conservative nature of entropy means that it obeys the equation,

$$m_1 \eta_1 + m_2 \eta_2 + m \delta \eta = m \eta. \quad (\text{A.16.5})$$

Here S_A , h and η are the values of Absolute Salinity, enthalpy and entropy of the final mixed fluid and $\delta \eta$ is the production of entropy, that is, the amount by which entropy is not conserved during the mixing process. Entropy η is now regarded as the functional form $\eta = \tilde{\eta}(S_A, h, p)$ and is expanded in a Taylor series of S_A and h about the values of S_A and h of the mixed fluid, retaining terms to second order in $[S_{A2} - S_{A1}] = \Delta S_A$ and in $[h_2 - h_1] = \Delta h$. Then η_1 and η_2 are evaluated and (A.16.4) and (A.16.5) used to find

$$\delta \eta = -\frac{1}{2} \frac{m_1 m_2}{m^2} \left\{ \tilde{\eta}_{hh} (\Delta h)^2 + 2 \tilde{\eta}_{hS_A} \Delta h \Delta S_A + \tilde{\eta}_{S_A S_A} (\Delta S_A)^2 \right\}. \quad (\text{A.16.6})$$

Shortly the production of entropy, Eqn. (A.16.6), will be quantified, but for now we ask what constraints the Second Law of Thermodynamics might place on the form of the Gibbs function $g(S_A, t, p)$ of seawater. The Second Law of Thermodynamics tells us that the entropy excess $\delta \eta$ must not be negative for all possible combinations of the differences in enthalpy and salinity between the two fluid parcels. From (A.16.6) this requirement implies the following three inequalities,

$$\tilde{\eta}_{hh} < 0, \quad \tilde{\eta}_{S_A S_A} < 0, \quad (\text{A.16.8})$$

$$\left(\tilde{\eta}_{hS_A} \right)^2 < \tilde{\eta}_{hh} \tilde{\eta}_{S_A S_A}, \quad (\text{A.16.9})$$

where the last requirement reflects the need for the discriminant of the quadratic in (A.16.6) to be negative. Since entropy is already a first order derivative of the Gibbs function, these constraints would seem to be three different constraints on various third order derivatives of the Gibbs function. In fact, we will see that they amount to only two rather well-known constraints on second order derivatives of the Gibbs function.

From the fundamental thermodynamic relation (A.7.1) we find that (where T is the absolute temperature, $T = T_0 + t$)

$$\tilde{\eta}_h = \left. \frac{\partial \eta}{\partial h} \right|_{S_A, p} = \frac{1}{T} \quad (\text{A.16.10})$$

$$\tilde{\eta}_{S_A} = \left. \frac{\partial \eta}{\partial S_A} \right|_{h, p} = -\frac{\mu}{T}, \quad (\text{A.16.11})$$

and from these relations the following expressions for the second order derivatives of $\tilde{\eta}$ can be found,

$$\tilde{\eta}_{hh} = \left. \frac{\partial^2 \eta}{\partial h^2} \right|_{S_A, p} = \left. \frac{\partial(1/T)}{\partial h} \right|_{S_A, p} = -\frac{1}{c_p T^2}, \quad (\text{A.16.12})$$

$$\tilde{\eta}_{S_A h} = \left. \frac{\partial^2 \eta}{\partial h \partial S_A} \right|_p = \left. \frac{\partial(-\mu/T)}{\partial h} \right|_{S_A, p} = -\frac{1}{c_p} \left(\frac{\mu}{T} \right)_T, \quad (\text{A.16.13})$$

$$\begin{aligned} \tilde{\eta}_{S_A S_A} &= \left. \frac{\partial^2 \eta}{\partial S_A^2} \right|_{h, p} = \left. \frac{\partial(-\mu/T)}{\partial S_A} \right|_{T, p} - \left. \frac{\partial(-\mu/T)}{\partial h} \right|_{S_A, p} \left. \frac{\partial h}{\partial S_A} \right|_{T, p} \\ &= -\frac{\mu_{S_A}}{T} - \frac{T^2}{c_p} \left[\left(\frac{\mu}{T} \right)_T \right]^2. \end{aligned} \quad (\text{A.16.14})$$

The last equation comes from regarding $\tilde{\eta}_{S_A}$ as $\tilde{\eta}_{S_A} = \tilde{\eta}_{S_A}(S_A, h[S_A, t, p], p)$.

The constraint (A.16.8) that $\tilde{\eta}_{hh} < 0$ simply requires (from (A.16.12)) that the isobaric heat capacity c_p is positive, or that $g_{TT} < 0$. Physically this constraint simply means that when you apply heat to a fluid parcel it warms up, rather than cools down.

The constraint (A.16.8) that $\tilde{\eta}_{S_A S_A} < 0$, requires (from (A.16.14)) that

$$g_{S_A S_A} > -\frac{T^3}{c_p} \left[\left(\frac{\mu}{T} \right)_T \right]^2, \quad (\text{A.16.15})$$

that is, the second derivative of the Gibbs function with respect to Absolute Salinity $g_{S_A S_A}$ must exceed some negative number. The constraint (A.16.9) that $(\tilde{\eta}_{h S_A})^2 < \tilde{\eta}_{hh} \tilde{\eta}_{S_A S_A}$ requires that (substituting from (A.16.12), (A.16.13) and (A.16.14))

$$\frac{g_{S_A S_A}}{T^3 c_p} > 0, \quad (\text{A.16.16})$$

and since the isobaric heat capacity must be positive, this requirement is that $g_{S_A S_A} > 0$, and so is more demanding than (A.16.15).

We conclude that while there are the three requirements (A.16.8) to (A.16.9) on the functional form of entropy $\eta = \tilde{\eta}(S_A, h, p)$ in order to satisfy the constraint of the Second Law of Thermodynamics that entropy be produced when water parcels mix, these three constraints are satisfied by the following two constraints on the form of the Gibbs function $g(S_A, t, p)$,

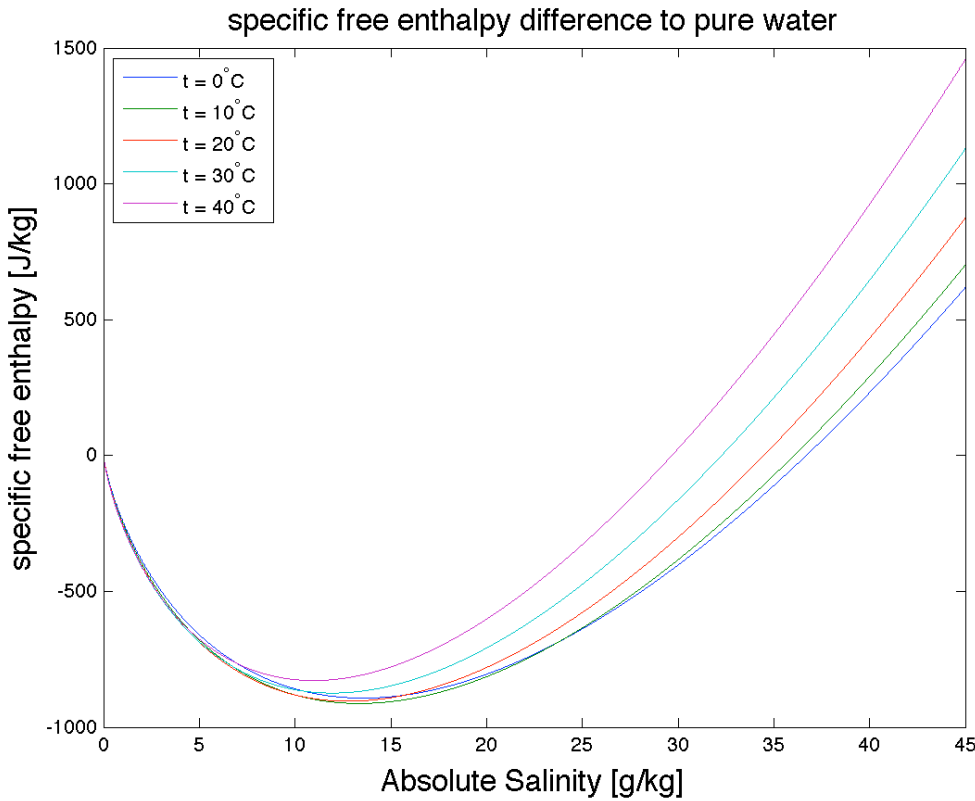
$$g_{TT} < 0 \quad (\text{A.16.17})$$

and

$$g_{S_A S_A} > 0. \quad (\text{A.16.18})$$

The Second Law of Thermodynamics does not impose any additional requirement on the cross derivatives $g_{S_A T}$ nor on any third order derivatives of the Gibbs function! (In any case, recall that $g_{S_A T}$ is completely arbitrary and unknowable.)

The constraint $g_{S_A S_A} > 0$ can be understood by considering the molecular diffusion of salt, which, in an isothermal ocean, is known to be directed down the gradient of chemical potential $\mu(S_A, t, p)/T$ (see Eqn. (B.21)). That is, the leading term in the molecular flux of salt is proportional to $-\nabla\mu$. Expanding $-\nabla\mu$ in terms of gradients of Absolute Salinity, of temperature, and of pressure, one finds that the first term is $-\mu_{S_A}\nabla S_A$ and in order to avoid an unstable explosion of salt one must have $\mu_{S_A} = g_{S_A S_A} > 0$. Hence the constraint (A.16.18) amounts to the requirement that the molecular diffusivity of salt is positive. The following figure shows that, indeed, $g_{S_A S_A} = \mu_{S_A} > 0$.



The two constraints (A.16.17) and (A.16.18) on the Gibbs function are well known in the thermodynamics literature. Landau and Lifshitz (1959) derive them on the basis of the contribution of molecular fluxes of heat and salt to the production of entropy (their equations 58.9 and 58.13). It is pleasing to obtain the same constraints on the seawater Gibbs function from the above Non-Equilibrium Thermodynamics approach of mixing fluid parcels since this approach involves turbulent mixing which is the type of mixing that dominates in the ocean; molecular diffusion has the complementary role of dissipating tracer variance.

When the mixing process occurs at $p = 0$, the expression (A.16.6) for the production of entropy can be expressed in terms of Conservative Temperature Θ (since Θ is simply proportional to h at $p = 0$) as follows (now entropy is taken to be the functional form $\eta = \hat{\eta}(S_A, \Theta)$)

$$\delta\eta = -\frac{1}{2} \frac{m_1 m_2}{m^2} \left\{ \hat{\eta}_{\Theta\Theta} (\Delta\Theta)^2 + 2\hat{\eta}_{\Theta S_A} \Delta\Theta \Delta S_A + \hat{\eta}_{S_A S_A} (\Delta S_A)^2 \right\}. \quad (\text{A.16.22})$$

The maximum production occurs when parcels of equal mass are mixed so that $\frac{1}{2} m_1 m_2 m^{-2} = \frac{1}{8}$ and we adopt this value in what follows.

To illustrate the magnitude of this non-conservation of entropy we first scale entropy by a dimensional constant so that the resulting variable (“entropic temperature”) has the value $25\text{ }^\circ\text{C}$ at $(S_A, \Theta) = (S_{SO}, 25\text{ }^\circ\text{C})$ and then Θ is subtracted. The result is contoured in $S_A - \Theta$ space in Figure A.16.1.

The fact that the variable in Figure A.16.1 is not zero over the whole $S_A - \Theta$ plane is because entropy is not a conservative variable. The non-conservative production of entropy can be read off this figure by selecting two seawater samples and mixing along the straight line between these parcels and then reading off the production (in $^\circ\text{C}$) of entropy from the figure. Taking the most extreme situation with one parcel at $(S_A, \Theta) = (0\text{ g kg}^{-1}, 0\text{ }^\circ\text{C})$ and the other at the warmest and saltiest corner of the figure, the production of η on mixing parcels of equal mass is approximately $0.9\text{ }^\circ\text{C}$.

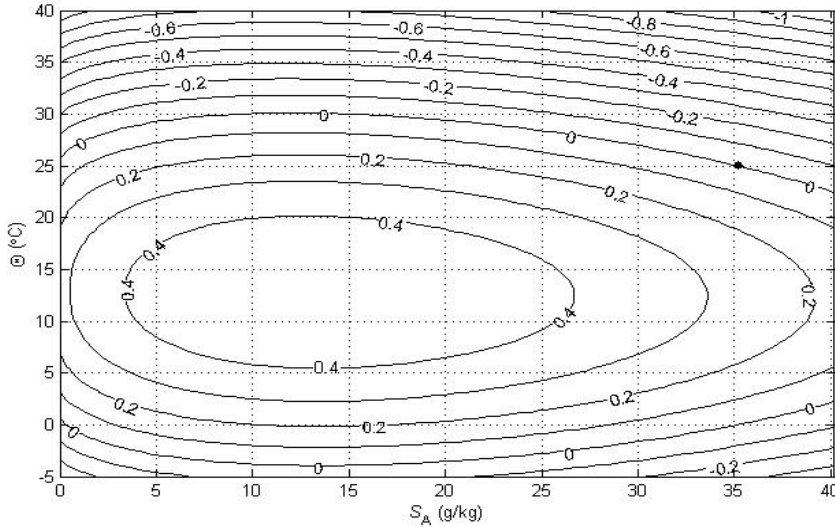


Figure A.16.1. Contours (in $^\circ\text{C}$) of a variable which illustrates the non-conservative production of entropy η in the ocean.

Since entropy can be expressed independently of pressure as a function of only Absolute Salinity and Conservative Temperature $\eta = \hat{\eta}(S_A, \Theta)$, and since at any pressure in the ocean both S_A and Θ may quite accurately be considered conservative variables, it is clear that the non-conservative production given by (A.16.22) and illustrated in Figure A.16.1 is very nearly equivalent to the slightly more accurate expression (A.16.6) which applies at any pressure. The only discrepancy between the production of entropy calculated from (A.16.22) and that from (A.16.6) is due to the very small non-conservative production of Θ at pressures other than zero (as well as the fact that both expressions contain only the second order terms in an infinite Taylor series). We have already seen that the non-conservation of entropy is much larger than the non-conservation of Conservative Temperature (by a factor of 1000 as it turns out).

Non-conservative production of potential temperature

When fluid parcels undergo irreversible and complete mixing at constant pressure, the thermodynamic quantities that are conserved during the mixing process are mass, Absolute Salinity and enthalpy. As in the case of entropy, we again consider two parcels being mixed without external input of heat or mass and the three equations that represent the conservation of these quantities are again Eqns. (A.16.2) – (A.16.4). The production of potential temperature during the mixing process is given by

$$m_1 \theta_1 + m_2 \theta_2 + m \delta\theta = m \theta. \quad (\text{A.17.1})$$

Enthalpy in the functional form $h = \tilde{h}(S_A, \theta, p)$ is expanded in a Taylor series of S_A and θ about the values S_A and θ of the mixed fluid, retaining terms to second order in $[S_{A2} - S_{A1}] = \Delta S_A$ and in $[\theta_2 - \theta_1] = \Delta\theta$. Then h_1 and h_2 are evaluated and Eqns. (A.16.4) and (A.17.1) used to find

$$\delta\theta = \frac{1}{2} \frac{m_1 m_2}{m^2} \left\{ \frac{\tilde{h}_{\theta\theta}}{\tilde{h}_\theta} (\Delta\theta)^2 + 2 \frac{\tilde{h}_{\theta S_A}}{\tilde{h}_\theta} \Delta\theta \Delta S_A + \frac{\tilde{h}_{S_A S_A}}{\tilde{h}_\theta} (\Delta S_A)^2 \right\}. \quad (\text{A.17.2})$$

The maximum production occurs when parcels of equal mass are mixed so that $\frac{1}{2} m_1 m_2 m^{-2} = \frac{1}{8}$. The “heat capacity” \tilde{h}_θ is not a strong function of θ but is a stronger function of S_A so the first term in the curly brackets in Eqn. (A.17.2) is generally small compared with the second term. Also, the third term in Eqn. (A.17.2) which causes the so-called “dilution heating”, is usually small compared with the second term. A typical value of $\tilde{h}_{\theta S_A}$ is approximately $-5.4 \text{ J kg}^{-1} \text{ K}^{-1} (\text{g kg}^{-1})^{-1}$ (see the dependence of isobaric heat capacity on S_A in [Figure 4](#) on page 1) so that an approximate expression for the production of potential temperature $\delta\theta$ is

$$\frac{\delta\theta}{\Delta\theta} \approx \frac{1}{4} \tilde{h}_{\theta S_A} \Delta S_A / \tilde{h}_\theta \approx -3.4 \times 10^{-4} (\Delta S_A / [\text{g kg}^{-1}]). \quad (\text{A.17.3})$$

The same form of the non-conservative production terms in Eqn. (A.17.2) also appears in the following turbulent evolution equation for potential temperature, in both the epineutral and vertical diffusion terms (Graham and McDougall, 2013). (See later for an explanation of the symbols that appear in this thickness-weighted averaged equation.)

$$\begin{aligned} \frac{d\hat{\theta}}{dt} &= \frac{\partial \hat{\theta}}{\partial t} \Big|_n + \hat{\mathbf{v}} \cdot \nabla_n \hat{\theta} + \tilde{\epsilon} \frac{\partial \hat{\theta}}{\partial z} = \tilde{\gamma}_z \nabla_n \cdot (\tilde{\gamma}_z^{-1} K \nabla_n \hat{\theta}) + (D\hat{\theta}_z)_z + \epsilon / \tilde{h}_\theta \\ &+ K \left(\frac{\tilde{h}_{\theta\theta}}{\tilde{h}_\theta} \nabla_n \hat{\theta} \cdot \nabla_n \hat{\theta} + 2 \frac{\tilde{h}_{\theta S_A}}{\tilde{h}_\theta} \nabla_n \hat{\theta} \cdot \nabla_n \hat{S}_A + \frac{\tilde{h}_{S_A S_A}}{\tilde{h}_\theta} \nabla_n \hat{S}_A \cdot \nabla_n \hat{S}_A \right) \\ &+ D \left(\frac{\tilde{h}_{\theta\theta}}{\tilde{h}_\theta} \hat{\theta}_z^2 + 2 \frac{\tilde{h}_{\theta S_A}}{\tilde{h}_\theta} \hat{\theta}_z \hat{S}_{Az} + \frac{\tilde{h}_{S_A S_A}}{\tilde{h}_\theta} (\hat{S}_{Az})^2 \right). \end{aligned} \quad (\text{A.17.4})$$

Since potential temperature $\theta = \hat{\theta}(S_A, \Theta)$ can be expressed independently of pressure as a function of only Absolute Salinity and Conservative Temperature, and since during turbulent mixing both S_A and Θ may be considered approximately conservative variables (see section A.18 below), it is clear that the non-conservative production given by (A.17.2) can be approximated by the corresponding production of potential temperature that would occur if the mixing had occurred at $p = 0$, namely

$$\delta\theta \approx \frac{1}{2} \frac{m_1 m_2}{m^2} \left\{ \frac{\tilde{\Theta}_{\theta\theta}}{\tilde{\Theta}_\theta} (\Delta\theta)^2 + 2 \frac{\tilde{\Theta}_{\theta S_A}}{\tilde{\Theta}_\theta} \Delta\theta \Delta S_A + \frac{\tilde{\Theta}_{S_A S_A}}{\tilde{\Theta}_\theta} (\Delta S_A)^2 \right\}, \quad (\text{A.17.5})$$

where the exact proportionality between potential enthalpy and Conservative Temperature $h^0 \equiv c_p^0 \Theta$ has been exploited. The maximum production occurs when parcels of equal mass are mixed so that $\frac{1}{2} m_1 m_2 m^{-2} = \frac{1}{8}$ and we adopt this value in what follows.

Equations (A.17.2) or (A.17.5) may be used to evaluate the non-conservative production of potential temperature due to mixing a pair of fluid parcels across a front at which there are known differences in salinity and temperature. The temperature difference $\theta - \Theta$ is contoured in **Figure A.17.1** and can be used to illustrate Eqn. (A.17.5). $\delta\theta$ can be read off this figure by selecting two seawater samples and mixing along the straight line between these parcels (along which both Absolute Salinity and Conservative Temperature are conserved) and then calculating the production (in $^{\circ}\text{C}$) of θ from the contoured values of $\theta - \Theta$. Taking the most extreme situation with one parcel at $(S_A, \Theta) = (0 \text{ g kg}^{-1}, 0 \text{ }^{\circ}\text{C})$ and the other at the warmest and saltiest corner of **Figure A.17.1**, the non-conservative production of θ on mixing parcels of equal mass is approximately $-0.55 \text{ }^{\circ}\text{C}$. This is to be compared with the corresponding maximum production of entropy, as discussed above in connection with Figure A.16.1, of approximately $0.9 \text{ }^{\circ}\text{C}$.

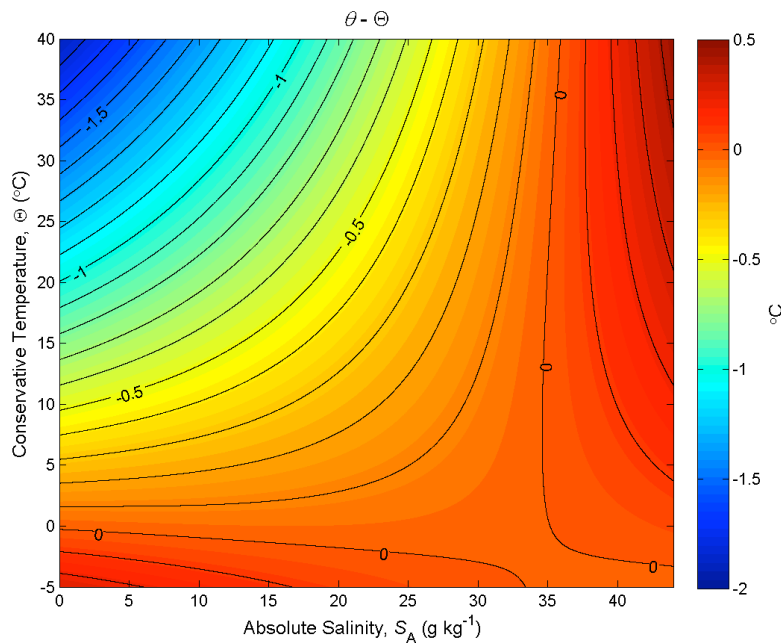


Figure A.17.1. Contours (in $^{\circ}\text{C}$) of the difference between potential temperature and Conservative Temperature $\theta - \Theta$. This plot illustrates the non-conservative production of potential temperature θ in the ocean.

How NOT to quantify the error involved in using potential temperature

If **Figure A.17.1** were to be used to quantify the errors in oceanographic practice incurred by assuming that θ is a conservative variable, one might select property contrasts that were typical of a prominent oceanic front and decide that because $\delta\theta$ is small at this one front, that the issue can be ignored. But the observed properties in the ocean result from a large and indeterminate number of such prior mixing events and the non-conservative production of θ accumulates during each of these mixing events, often in a sign-definite fashion. How can we possibly estimate the error that is made by treating potential temperature as a conservative variable during all of these unknowably many past individual mixing events?

How to quantify the error involved in using potential temperature

This seemingly difficult issue is partially resolved by considering what is actually done in ocean models today. These models carry a temperature conservation equation that does not have non-conservative source terms, so that the model's temperature variable is best interpreted as being Θ . If an ocean model is written with potential temperature θ as the prognostic temperature variable rather than Conservative Temperature Θ , and is run with the same constant value of the isobaric specific heat capacity c_p^0 , the neglect of the non-conservative source terms that should appear in the prognostic equation for θ means that such an ocean model incurs errors in the model output. These errors will depend on the nature of the surface boundary condition; for flux boundary conditions the errors are as shown in [Figure A.17.1](#), because in this case the model's temperature variable is actually Conservative Temperature Θ but has been interpreted and initialized incorrectly as potential temperature θ .

The contoured values of temperature difference in [Figure A.17.1](#) encapsulate the accumulated non-conservative production that has occurred during all the many mixing processes that have lead to the ocean's present state. The maximum such error for η is approximately -1.0 °C (from [Figure A.16.1](#)) while for θ the maximum error is approximately -1.8 °C (from [Figure A.17.1](#)). From the curvature of the isolines on [Figure A.17.1](#) it is clear that the non-conservative production of θ takes both positive and negative signs.

Here is an enlarged view of $\theta - \Theta$ on the $S_A - \Theta$ diagram, and also of the error involved with using another previous suggestion for the "heat content" of seawater, $\theta c_p(S_A, \theta, p) / c_p^0$.

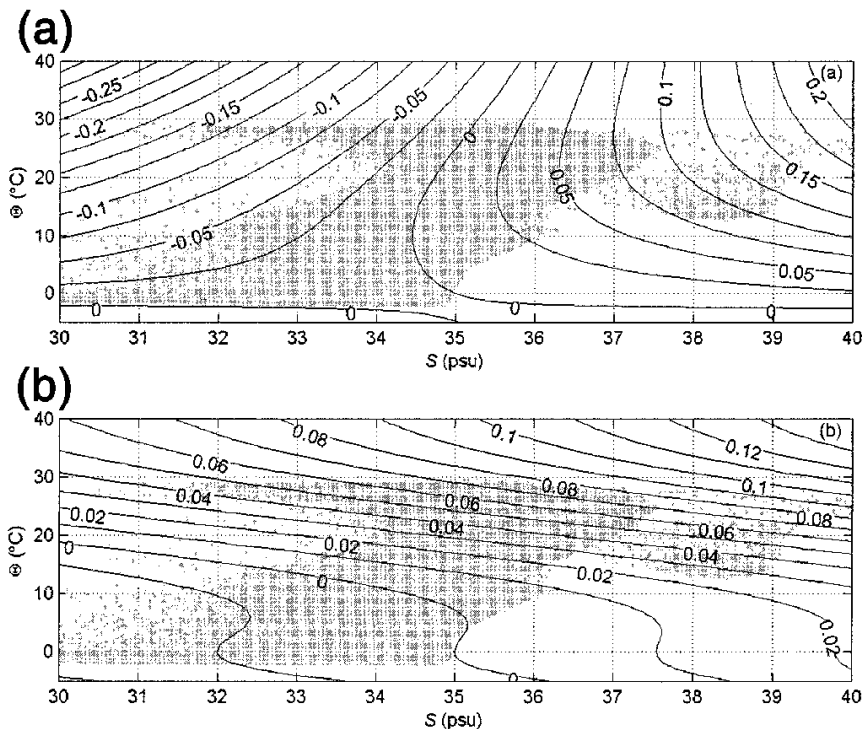


FIG. 3. Contours of (a) $\theta - \Theta$ and of (b) $C_p(S, \theta, 0)\theta / C_p^0 - \Theta$ in a smaller range of salinity than in Figs. 1 and 4. Panel (a) illustrates the error in regarding $C_p^0\theta$ as heat content; panel (b) illustrates the error in regarding $C_p(S, \theta, 0)\theta$ as heat content, in both cases measured in temperature units. The background cloud of points illustrate where there is data from somewhere in the World Ocean.

One percent of the data at the sea surface of the world ocean have values of $\theta - \Theta$ that lie outside a range that is $0.25\text{ }^\circ\text{C}$ wide (see [Figure A.13.1](#)), implying that this is the magnitude of the error incurred by ocean models when they treat θ as a conservative quantity. To put a temperature difference of $0.25\text{ }^\circ\text{C}$ in context, this is the typical difference between *in situ* and potential temperatures for a pressure difference of 2500 dbar, and it is approximately 100 times as large as the typical differences between t_{90} and t_{68} in the ocean.

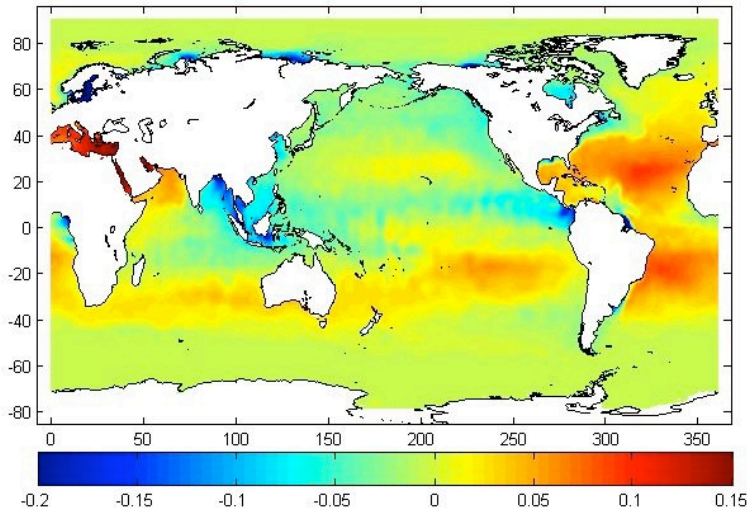
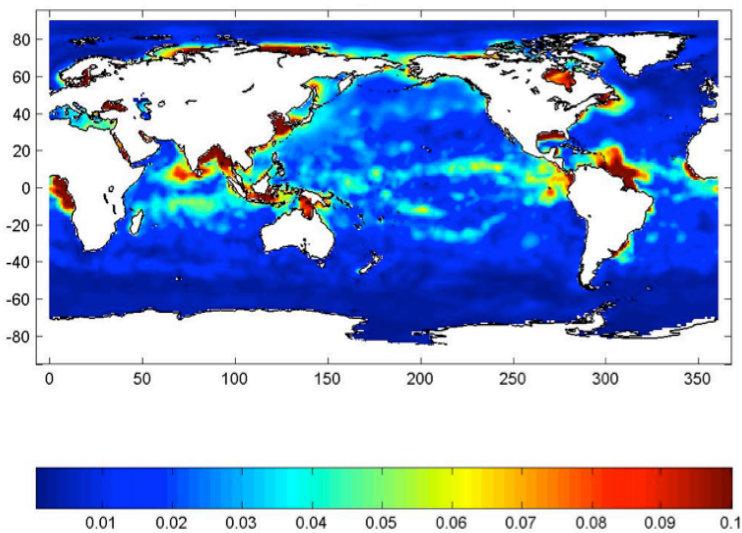


Figure A.13.1. The difference $\theta - \Theta$ (in $^\circ\text{C}$) between potential temperature θ and Conservative Temperature Θ at the sea surface of the annually-averaged atlas of Gouretski and Koltermann (2004).



The maximum value of the seasonal variation in $|\theta - \Theta|$ (in $^\circ\text{C}$) at the sea surface throughout the annual cycle of the hydrographic atlas of Gouretski and Koltermann (2004).

Review of the recent lectures

We examined the process of turbulent mixing and showed that in order for the Second Law of Thermodynamics to be obeyed (and entropy to be always produced), there are only two constraints on the form of the Gibbs function, namely

$$g_{TT} < 0 \tag{A.16.17}$$

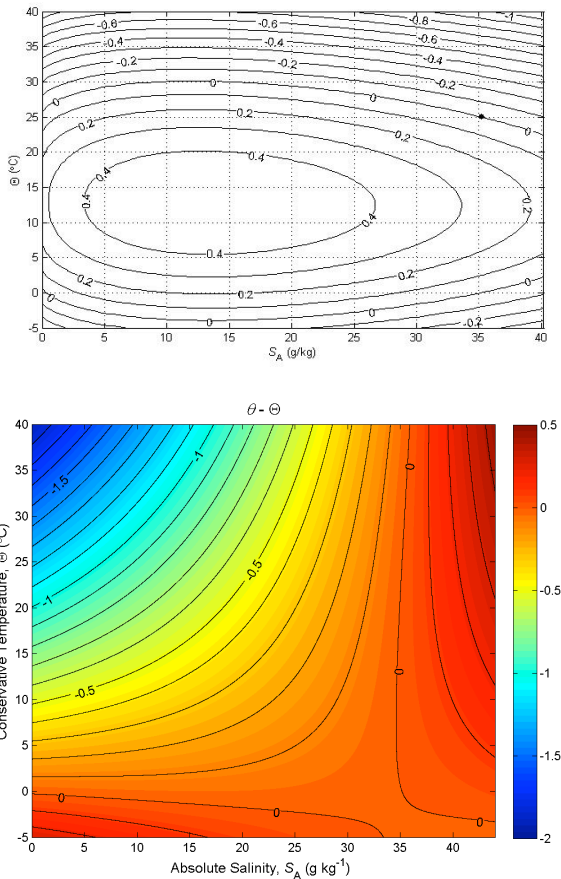
and

$$g_{S_A S_A} > 0. \tag{A.16.18}$$

These constraints mean that (i) the fluid must increase its temperature when it is heated, and (ii) the solute should not spontaneously “unmix”. These constraints on the Gibbs function are well known from considerations of molecular fluxes. It is encouraging that they emerge also from the turbulent mixing process, which happens quite independently of the form of the molecular fluxes.

We considered the turbulent mixing of pairs of seawater parcels that had finite amplitude differences of Absolute Salinity and of temperature. By employing a Taylor series analysis, we were able to get an expression for the non-conservative production of entropy and of potential temperature when the parcels are mixed to uniformity.

We were able to illustrate the non-conservative production of entropy and of potential temperature, when mixing occurs between pairs of fluid parcels, on the following carefully-constructed diagrams.



We then showed that these diagrams are the measure of the error involved with assuming that entropy or potential temperature is conserved in the ocean. Because of the unknowably many mixing events in the life-history of a seawater parcel, these diagrams illustrate the sum of these non-conservative sources in the past, over many different mixing events over the past 1000 years.

Non-conservative production of specific volume

Specific volume is expressed as a function of Absolute Salinity S_A , specific enthalpy h and pressure as $v = \tilde{v}(S_A, h, p)$ and the same mixing process between two fluid parcels is considered as in the previous appendices. Mass, salt and enthalpy are conserved during the turbulent mixing process (Eqns. (A.16.2) - (A.16.4)) while the non-conservative nature of specific volume means that it obeys the equation,

$$m_1 v_1 + m_2 v_2 + m \delta v = m v. \quad (\text{A.19.1})$$

Specific volume is expanded in a Taylor series of S_A and h about the values of S_A and h of the mixed fluid at pressure p , retaining terms to second order in $[S_{A2} - S_{A1}] = \Delta S_A$ and in $[h_2 - h_1] = \Delta h$. Then v_1 and v_2 are evaluated and (A.19.1) is used to find

$$\begin{aligned} \delta v &= -\frac{1}{2} \frac{m_1 m_2}{m^2} \left\{ \tilde{v}_{hh} (\Delta h)^2 + 2 \tilde{v}_{hS_A} \Delta h \Delta S_A + \tilde{v}_{S_A S_A} (\Delta S_A)^2 \right\} \\ &\approx -\frac{1}{2} \frac{m_1 m_2}{m^2} \left\{ \hat{v}_{\Theta\Theta} (\Delta\Theta)^2 + 2 \hat{v}_{\Theta S_A} \Delta\Theta \Delta S_A + \hat{v}_{S_A S_A} (\Delta S_A)^2 \right\}. \end{aligned} \quad (\text{A.19.2})$$

The non-conservative destruction of specific volume of Eqn. (A.19.2) is illustrated in **Figure A.19.1** for mixing at $p = 0$ dbar. The quantity contoured on this figure is formed as follows. First the linear function of S_A is found that is equal to specific volume at $(S_A=0, \Theta=0^\circ\text{C})$ and at $(S_A=35.16504 \text{ g kg}^{-1}, \Theta=0^\circ\text{C})$. This linear function of S_A is subtracted from v and the result is scaled to equal exactly 25°C at $(S_A=35.16504 \text{ g kg}^{-1}, \Theta=25^\circ\text{C})$. The variable that is contoured in Figure A.19.1 is the difference between this scaled linear combination of v and S_A , and Conservative Temperature. This figure allows the non-conservative nature of specific volume to be understood in temperature units. The mixing of extreme fluid parcels on Figure A.19.1 causes the same decrease in specific volume as a cooling of approximately 10°C , which is approximately 4000 times larger than the corresponding non-conservative production of Θ at 600dbar (from Figure A.18.1).

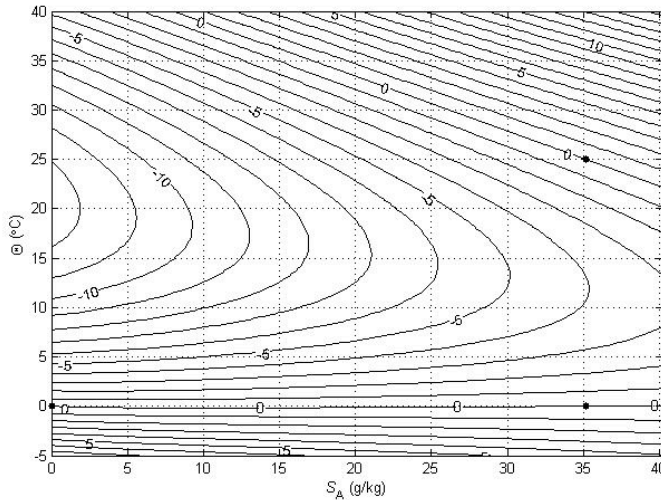


Figure A.19.1. Contours (in $^\circ\text{C}$) of a variable that is used to illustrate the non-conservative production of specific volume at $p = 0$ dbar. The three points that are forced to be zero are shown with black dots.

From Eqn. (A.19.2) it follows that specific volume is always destroyed by turbulent mixing processes if $\tilde{v}_{hh} > 0$, $\tilde{v}_{S_A S_A} > 0$ and $(\tilde{v}_{hS_A})^2 < \tilde{v}_{S_A S_A} \tilde{v}_{hh}$, and Graham and McDougall (2013) have shown that these conditions are satisfied over the full TEOS-10 ranges of salinity, temperature and pressure by both the full TEOS-10 Gibbs function $g(S_A, t, p)$ and by the polynomial expression for

specific volume $\hat{v}(S_A, \Theta, p)$ of the Gibbs SeaWater (GSW) Oceanographic Toolbox. Note that in contrast to the case of specific volume, the non-conservation of density is not sign-definite. That is, while turbulent mixing always destroys specific volume, it does not always produce density $\rho = v^{-1}$.

Specific volume is the more appropriate variable to consider in this regard because it is volume per unit mass, and mass (which is on the denominator of specific volume $v = V/M$) is a conservative quantity whereas volume is not. So if one considers the non-conservative nature of density, $\rho = v^{-1} = M/V$, then one is actually enquiring about the non-conservation of the reciprocal of a non-conservative quantity, namely the reciprocal of volume V (since mass M is a conservative quantity). This explains how (but not why) specific volume is always destroyed by a turbulent mixing process while density is not always produced non-conservatively by the same turbulent mixing process. I do not know if this is a property that is specific to seawater (and pure water) or if there is a fundamental thermodynamic reason why this should be the case for all fluids; to date I have been unable to find a thermodynamic principle that would ensure that it would be the case for all fluids [I should look for a counterexample fluid]. Specific volume (rather than density) is the variable that naturally appears in the FTR as Pdv and vdP , and for good reason, since like the other variables that appear in the FTR such as internal energy, enthalpy, entropy and Absolute Salinity, specific volume is a “per unit mass” variable, not a “per unit volume” variable.

The fact that turbulent mixing at constant pressure always destroys specific volume v also implies that internal energy u is always produced by this turbulent mixing at constant pressure. To see this we start with the First Law of Thermodynamics, Eqn. (B.19),

$$\rho \left(\frac{dh}{dt} - v \frac{dP}{dt} \right) = \rho \left(\frac{du}{dt} + (p + P_0) \frac{dv}{dt} \right) = \rho \left((T_0 + t) \frac{d\eta}{dt} + \mu \frac{dS_A}{dt} \right) \quad (\text{B.19})$$

$$= -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon,$$

and cast it in divergence form so that the First Law of Thermodynamics becomes

$$\left(\rho h \right)_t + \nabla \cdot (\rho \mathbf{u} h) - \frac{dP}{dt} = \left(\rho u \right)_t + \nabla \cdot (\rho \mathbf{u} u) + \frac{(p + P_0)}{v} \frac{dv}{dt} \quad (\text{B.19a})$$

$$= -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon.$$

The turbulent mixing at constant pressure conserves enthalpy and each of the parts of this equation is zero for a control volume that encircles the mixing region. Since specific volume is always destroyed by turbulent mixing, that is $dv < 0$, the second part of Eqn. (B.19a) implies that internal energy, u , is always produced by turbulent mixing at constant pressure. Moreover, the amount of production of internal energy is proportional to the absolute pressure $(p + P_0)$!

Non-conservative production of Conservative Temperature

When fluid parcels undergo irreversible and complete mixing at constant pressure, the thermodynamic quantities that are conserved are mass, Absolute Salinity and enthalpy. As above we consider two parcels being mixed without external input of heat or mass, and the three equations that represent the conservation of these quantities are Eqns. (A.16.2) – (A.16.4). Potential enthalpy h^0 and Conservative Temperature Θ are not exactly conserved during the mixing process and the production of Θ is given by

$$m_1 \Theta_1 + m_2 \Theta_2 + m \delta\Theta = m \Theta. \quad (\text{A.18.1})$$

Enthalpy in the functional form $h = \hat{h}(S_A, \Theta, p)$ is expanded in a Taylor series of S_A and Θ about the values S_A and Θ of the mixed fluid, retaining terms to second order in $[S_{A2} - S_{A1}] = \Delta S_A$ and in $[\Theta_2 - \Theta_1] = \Delta\Theta$. Then h_1 and h_2 are evaluated and Eqns. (A.16.4) and (A.18.1) are used to find

$$\delta\Theta = \frac{1}{2} \frac{m_1 m_2}{m^2} \left\{ \frac{\hat{h}_{\Theta\Theta}}{\hat{h}_\Theta} (\Delta\Theta)^2 + 2 \frac{\hat{h}_{\Theta S_A}}{\hat{h}_\Theta} \Delta\Theta \Delta S_A + \frac{\hat{h}_{S_A S_A}}{\hat{h}_\Theta} (\Delta S_A)^2 \right\}. \quad (\text{A.18.2})$$

Graham and McDougall (2013) have shown that the same form of the non-conservative production terms in Eqn. (A.18.2) also appears in the following turbulent evolution equation for Conservative Temperature, in both the epineutral and vertical diffusion terms (see appendix A.21 for an explanation of the symbols that appear in this thickness-weighted averaged equation),

$$\begin{aligned} \frac{d\hat{\Theta}}{dt} &= \left. \frac{\partial\hat{\Theta}}{\partial t} \right|_n + \hat{\mathbf{v}} \cdot \nabla_n \hat{\Theta} + \tilde{\epsilon} \frac{\partial\hat{\Theta}}{\partial z} = \tilde{\gamma}_z \nabla_n \cdot (\tilde{\gamma}_z^{-1} K \nabla_n \hat{\Theta}) + (D\hat{\Theta}_z)_z + \epsilon / \hat{h}_\Theta \\ &+ K \left(\frac{\hat{h}_{\Theta\Theta}}{\hat{h}_\Theta} \nabla_n \hat{\Theta} \cdot \nabla_n \hat{\Theta} + 2 \frac{\hat{h}_{\Theta S_A}}{\hat{h}_\Theta} \nabla_n \hat{\Theta} \cdot \nabla_n \hat{S}_A + \frac{\hat{h}_{S_A S_A}}{\hat{h}_\Theta} \nabla_n \hat{S}_A \cdot \nabla_n \hat{S}_A \right) \\ &+ D \left(\frac{\hat{h}_{\Theta\Theta}}{\hat{h}_\Theta} \hat{\Theta}_z^2 + 2 \frac{\hat{h}_{\Theta S_A}}{\hat{h}_\Theta} \hat{\Theta}_z \hat{S}_{Az} + \frac{\hat{h}_{S_A S_A}}{\hat{h}_\Theta} (\hat{S}_{Az})^2 \right). \end{aligned} \quad (\text{A.18.3})$$

The reasoning behind the derivation of this equation is as follows. A single turbulent mixing event is considered, with the mixing event occurring at the pressure p^m . A new potential enthalpy variable h^m is constructed with the reference pressure of the potential enthalpy being p^m . During the turbulent mixing event at p^m both enthalpy h and the potential enthalpy variable h^m are conserved. Moreover, since h^m is a “potential” variable, it is unchanged as seawater parcels are advected vertically to arrive at the pressure p^m where they are subject to turbulent mixing. Hence, for the purpose of analyzing the turbulent mixing process at pressure p^m , h^m behaves as both a “potential” variable and a conservative variable. This ensures that the epineutral turbulent flux of h^m and the small-scale isotropic diffusion h^m can be treated in the same way as the corresponding turbulent fluxes of an ordinary conservative variable such as Preformed Salinity (we outline this averaging procedure on pages 96 – 99 of these lectures below).

This enables the appropriate averaging of the instantaneous conservation equation of h^m to be performed and the final step to arrive at Eqn. (A.18.3) above is to relate the gradients of h^m to the corresponding gradients of Absolute Salinity and Conservative Temperature using the functional relationship $h^m = \hat{h}(S_A, \Theta, p^m)$. This reasoning and the derivation of Eqn. (A.18.3) can be found in sections 3(b) and 3(c) of Graham and McDougall (2103).

In order to evaluate the partial derivatives in Eqns. (A.18.2) and (A.18.3), first write enthalpy in terms of potential enthalpy ($c_p^0 \Theta$) using Eqn. (3.2.1), as

$$h = \hat{h}(S_A, \Theta, p) = c_p^0 \Theta + \int_{P_0}^P \hat{v}(S_A, \Theta, p') dP'. \quad (\text{A.18.4})$$

Below we will use the relevant thermal expansion coefficient α^\ominus and saline contraction coefficient β^\ominus , defined with respect to Absolute Salinity and Conservative Temperature by

$$\alpha^\ominus = -\frac{1}{\rho} \frac{\partial \rho}{\partial \Theta} \Big|_{S_A, p} \quad \text{and} \quad \beta^\ominus = \frac{1}{\rho} \frac{\partial \rho}{\partial S_A} \Big|_{\Theta, p}. \quad (\text{2.18.3}), (\text{2.19.3})$$

Eqn. (A.18.4) is now differentiated with respect to Θ giving

$$h_{\Theta} \Big|_{S_A, p} = \hat{h}_{\Theta} = c_p^0 + \int_{P_0}^P \hat{v}_{\Theta}(S_A, \Theta, p') dP' = c_p^0 + \int_{P_0}^P \alpha^\ominus / \rho dP'. \quad (\text{A.18.5})$$

The right-hand side of Eqn. (A.18.5) scales as $c_p^0 + \rho^{-1}(P-P_0)\alpha^\ominus$, which is more than c_p^0 by only about $0.0015c_p^0$ for $(P-P_0)$ as large as 4×10^7 Pa (4,000 dbar). Hence, to a very good approximation, \hat{h}_{Θ} in Eqns. (A.18.2) and (A.18.3) may be taken to be simply c_p^0 .

As an exercise, use Eqn. (A.18.4) to show that an adiabatic and isohaline pressure change of 10^7 Pa (1,000 dbar) causes a change in enthalpy h as large as does an isobaric change in temperature of about 2.5°C . This is because enthalpy h does not possess the ‘‘potential’’ property.

Why is the approximation $\hat{h}_{\Theta} \approx c_p^0$ so accurate when the difference between enthalpy, h , and potential enthalpy, h^0 , as given by Eqns. (3.2.1) and (A.18.4), scales as $\rho^{-1}(P-P_0)$ which is as large as typical values of potential enthalpy?

The reason is that the integral in Eqns. (3.2.1) or (A.18.4) is dominated by the integral of the mean value of ρ^{-1} , so causing a significant offset between h and h^0 as a function of pressure but not affecting the partial derivative \hat{h}_{Θ} which is taken at fixed pressure. Even the dependence of specific volume on pressure alone does not affect \hat{h}_{Θ} . It is only the dependence of specific volume on Θ at fixed pressure that affects \hat{h}_{Θ} .

Recall from Eqn. (A.11.15), namely

$$\hat{h}_{\Theta} \Big|_{S_A, p} = \frac{(T_0 + t)}{(T_0 + \theta)} c_p^0. \quad (\text{A.11.15})$$

and combining this with (A.18.5) we see that

$$\frac{(t - \theta)}{(T_0 + \theta)} c_p^0 = \int_{P_0}^P \alpha^\ominus / \rho dP' = \int_{P_0}^P \hat{v}_{\Theta}(S_A, \Theta, p') dP' \quad (\text{A.18.5a})$$

which is an interesting relationship between a temperature difference on the left-hand side (which is related directly to the functional dependence of entropy on *in situ* temperature and pressure) and a pressure integral of essentially the thermal expansion coefficient on the right-hand side. We actually go between *in situ* and potential temperatures by solving the identity $\eta(S_A, \theta, p_r) = \eta(S_A, t, p)$, but Eqn. (A.18.5a) shows that we could instead calculate the difference between the *in situ* and potential temperatures from knowledge only of $\hat{v}(S_A, \Theta, p)$.

The second order derivatives of \hat{h} are needed in Eqns. (A.18.2) and (A.18.3), and these can be estimated by differentiating Eqn. (A.18.4) or (A.18.5), so that, for example,

$$\hat{h}_{\Theta\Theta} = \int_{P_0}^P \hat{v}_{\Theta\Theta} dP' = \int_{P_0}^P (\alpha^\ominus / \rho)_{\Theta} dP', \quad (\text{A.18.6})$$

so that we may write Eqn. (A.18.2) approximately as (assuming $m_1 = m_2$)

$$\delta\Theta \approx \frac{(P-P_0)}{8c_p^0} \left\{ \hat{v}_{\Theta\Theta} (\Delta\Theta)^2 + 2\hat{v}_{S_A\Theta} \Delta\Theta \Delta S_A + \hat{v}_{S_A S_A} (\Delta S_A)^2 \right\}. \quad (\text{A.18.7})$$

This equation is approximate because the variation of $\hat{v}_{\Theta\Theta}$, $\hat{v}_{\Theta S_A}$ and $\hat{v}_{S_A S_A}$ with pressure has been ignored. The dominant term in Eqn. (A.18.7) is usually the term in $\hat{v}_{\Theta\Theta}$ and from Eqn. (A.19.2) above we see that $\delta\Theta$ is approximately proportional to the non-conservative destruction of specific volume at fixed pressure δv caused by the “cabbeling” non-linearities in the equation of state (McDougall, 1987b), so that

$$\delta\Theta \approx \frac{(P-P_0)}{8c_p^0} \hat{v}_{\Theta\Theta} (\Delta\Theta)^2 \approx -\frac{(P-P_0)}{c_p^0} \delta v. \quad (\text{A.18.8})$$

The production of Θ causes an increase in Conservative Temperature and a consequent decrease in density of $-\rho\alpha^\Theta\delta\Theta$. The ratio of this change in density (using Eqn. (A.18.7)) to that caused by cabbeling (from Eqn. (A.19.2) and using $\delta\rho \approx -\rho^2\delta v$) is $-(P-P_0)\alpha^\Theta/\rho c_p^0$ which is about 0.0015 for a value of $(P-P_0)$ of 40 MPa. Hence it is clear that “cabbeling” has a much larger effect on density than does the non-conservation of Θ . Nevertheless, it is interesting to note from Eqn. (A.18.7) that the non-conservative production of Θ is approximately proportional to the product of sea pressure and the strength of cabbeling, δv .

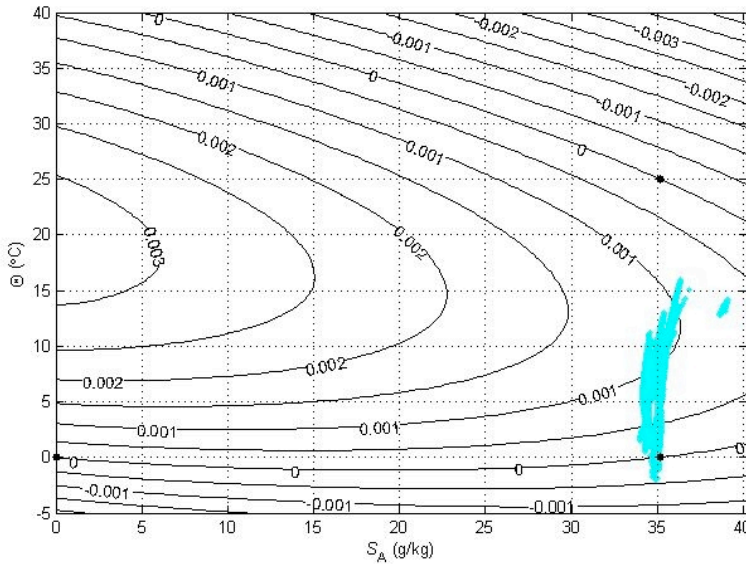


Figure A.18.1. Contours (in °C) of a variable that is used to illustrate the non-conservative production of Conservative Temperature Θ at $p = 600$ dbar. The cloud of points show where most of the oceanic data reside at $p = 600$ dbar. The three points that are forced to be zero are shown with black dots.

At the sea surface Conservative Temperature Θ is totally conserved ($\delta\Theta = 0$). The expression for the non-conservative production of Conservative Temperature, $\delta\Theta$, increases almost linearly with pressure (see Eqn. (A.18.7)) but at large pressures the range of temperature and salinity in the ocean decreases, and from the above equations it is clear that the magnitude of $\delta\Theta$ is proportional to the square of the temperature and salinity contrasts. McDougall (2003) concluded that the production $\delta\Theta$ between extreme seawater parcels at each pressure is largest at 600 dbar. The magnitude of the non-conservative production of Conservative Temperature, $\delta\Theta$, is illustrated in **Figure A.18.1** for data at this pressure.

The quantity contoured on this figure is the difference between Θ and the following totally conservative quantity at $p = 600$ dbar. This conservative quantity was constructed by taking the conservative property enthalpy h at this pressure and adding the linear function of S_A which makes the result equal to zero at $(S_A = 0, \Theta = 0^\circ\text{C})$ and at $(S_A = 35.165\text{ }04\text{ g kg}^{-1}, \Theta = 0^\circ\text{C})$. This quantity is

then scaled so that it becomes exactly $25\text{ }^\circ\text{C}$ at $(S_A = 35.165\ 04\ \text{g kg}^{-1}, \Theta = 25\text{ }^\circ\text{C})$. In this manner the quantity that is contoured in Figure A.18.1 has units of $^\circ\text{C}$ and represents the amount by which Conservative Temperature Θ is not a totally conservative variable at a pressure of 600 dbar. The maximum amount of production by mixing seawater parcels at the boundaries of Figure A.18.1 is about $4 \times 10^{-3}\text{ }^\circ\text{C}$ although the range of values encountered in the real ocean at this pressure is actually quite small, as indicated in Figure A.18.1.

From the curvature of the isolines on Figure A.18.1 it is clear that the non-conservative production of Conservative Temperature at $p = 600$ dbar is positive, so that an ocean model that ignores this production of Conservative Temperature will slightly underestimate Θ . From Eqn. (A.18.2) one sees the non-conservative production of Conservative Temperature is always positive if $\hat{h}_{\Theta\Theta} > 0$, $\hat{h}_{S_A S_A} > 0$ and $(\hat{h}_{\Theta S_A})^2 < \hat{h}_{\Theta\Theta} \hat{h}_{S_A S_A}$, and Graham and McDougall (2013) have shown that these requirements are met everywhere in the full TEOS-10 ranges of salinity, temperature and pressure for both the full TEOS-10 Gibbs function $g(S_A, t, p)$ and by the polynomial expression for specific enthalpy $\hat{h}(S_A, \Theta, p)$ of the Gibbs SeaWater (GSW) Oceanographic Toolbox.

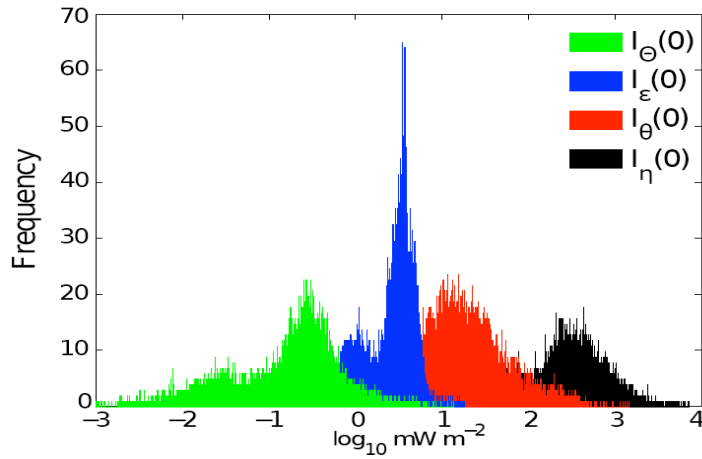
Depth-integrated measures of the non-conservation of θ , η and Θ

Graham and McDougall (2013) have derived the evolution equations for potential temperature, Conservative Temperature and specific entropy in a turbulent ocean, with the one for Conservative Temperature being

$$\begin{aligned} \frac{d\hat{\Theta}}{dt} = \frac{\partial\hat{\Theta}}{\partial t} \Big|_n + \hat{\mathbf{v}} \cdot \nabla_n \hat{\Theta} + \tilde{e} \frac{\partial\hat{\Theta}}{\partial z} = \gamma_z \nabla_n \cdot (\gamma_z^{-1} K \nabla_n \hat{\Theta}) + (D\hat{\Theta}_z)_z + \varepsilon / \hat{h}_\Theta \\ + K \left(\frac{\hat{h}_{\Theta\Theta}}{\hat{h}_\Theta} \nabla_n \hat{\Theta} \cdot \nabla_n \hat{\Theta} + 2 \frac{\hat{h}_{\Theta S_A}}{\hat{h}_\Theta} \nabla_n \hat{\Theta} \cdot \nabla_n \hat{S}_A + \frac{\hat{h}_{S_A S_A}}{\hat{h}_\Theta} \nabla_n \hat{S}_A \cdot \nabla_n \hat{S}_A \right) \quad (\text{A.18.3}) \\ + D \left(\frac{\hat{h}_{\Theta\Theta}}{\hat{h}_\Theta} \hat{\Theta}_z^2 + 2 \frac{\hat{h}_{\Theta S_A}}{\hat{h}_\Theta} \hat{\Theta}_z \hat{S}_{Az} + \frac{\hat{h}_{S_A S_A}}{\hat{h}_\Theta} (\hat{S}_{Az})^2 \right). \end{aligned}$$

The red terms on the second and third lines of this equation are the non-conservative production terms and they can be evaluated in an ocean model.

One way of quantifying the magnitude of these red terms in Eqn. (A.18.3) is to vertically integrate these terms and to express this vertical integral as a vertical heat flux. That is, consider a vertical ocean water column that is the full depth of the ocean and is one square meter in area. In terms of its effect on the depth-integrated heat budget, the vertical integral of the red source terms is equivalent to an extra air-sea or geothermal heat flux. This equivalent surface flux is shown as a histogram for the whole world ocean in the figure below.



The 95 percentile largest values of these four error measures is shown below.

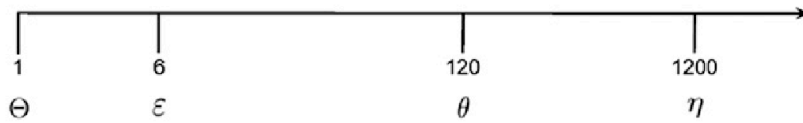


FIG. 10. The 95% error occurrences of the depth-integrated nonconservative source terms for ϵ , θ , and η to that of Θ (10^{-3} W m^{-2}) on a logarithmic scale.

This demonstrates that the non-conservative source terms of potential temperature are two orders of magnitude larger than those for Conservative Temperature, and that the dissipation of kinetic energy is almost an order of magnitude larger than the non-conservative source terms in the evolution equation for Conservative Temperature.

To put this in perspective, the mean geothermal heat flux is $\sim 86.4 \text{ mW m}^{-2}$, and the extra surface heat flux that the planet is receiving now from global warming is $\sim 1.5 \text{ W m}^{-2}$.

Keeping track of “heat” in the ocean; advection and diffusion of heat

We have seen that the First Law of Thermodynamics is practically equivalent to the conservation equation for Conservative Temperature Θ . We have emphasized that this means that the advection of “heat” is very accurately given as the advection of $c_p^0 \Theta$. In this way $c_p^0 \Theta$ can be regarded as the “heat content” per unit mass of seawater. The error involved with making this association is approximately 1% of the error in assuming that either $c_p^0 \theta$ or $c_p(S_A, \theta, 0 \text{ dbar}) \theta$ is the “heat content” per unit mass of seawater.

A flux of heat across the sea surface at a sea pressure of 0 dbar is identical to the flux of potential enthalpy which is exactly equal to c_p^0 times the flux of Conservative Temperature Θ . By contrast, the same heat flux across the sea surface changes potential temperature θ in inverse proportion to $c_p(S_A, \theta, 0)$ which varies by 5% at the sea surface, depending mainly on salinity.

The First Law of Thermodynamics can be approximated as

$$\rho c_p^0 \frac{d\Theta}{dt} = c_p^0 (\rho \Theta)_t + c_p^0 \nabla \cdot (\rho \Theta \mathbf{u}) \approx -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon, \quad (3.23.1)$$

with an error in Θ that is approximately one percent of the error incurred by treating either $c_p^0 \theta$ or $c_p(S_A, \theta, 0) \theta$ as the “heat content” of seawater, and approximately 10% of the error in ignoring the dissipation rate of turbulent kinetic energy term $\rho \varepsilon$ in this equation. Equation (3.23.1) is exact at 0 dbar.

Because the left-hand side of the First Law of Thermodynamics, Eqn. (3.23.1), can be written as density times the material derivative of $c_p^0 \Theta$ it follows that Θ can be treated as a conservative variable in the ocean and that $c_p^0 \Theta$ is transported by advection and mixed by turbulent epineutral and dianeutral diffusion as though it is the “heat content” of seawater. For example, the advective meridional flux of “heat” is the area integral of $\rho v h^0 = \rho v c_p^0 \Theta$ (here v is the northward velocity).

Some have argued that because enthalpy is unknown up to a linear function of salinity, it is only possible to talk of a flux of “heat” through an ocean section if the fluxes of mass and salt through the ocean section are both zero. This opinion seems to be widely held, but it is incorrect. The fact that $c_p^0 \Theta$ is unknowable up to a linear function of S_A does not affect the usefulness of h^0 or $c_p^0 \Theta$ as measures of “heat content”:- the difference between the meridional (i.e. northward) fluxes of $c_p^0 \Theta$ across two latitudes is equal to the area-integrated air-sea and geothermal heat fluxes between these latitudes (after allowing for any unsteady accumulation of $c_p^0 \Theta$ in the volume), irrespective of whether there are non-zero fluxes of mass or salt across the sections. This powerful result follows directly from the fact that $c_p^0 \Theta$ is taken to be a conservative variable, obeying the simple conservation statement Eqn. (3.23.1) (modulo the dissipation of kinetic energy, $\rho \varepsilon$). No one would doubt the sensibleness of calculating the meridional flux of a general passive tracer that obeyed such a conservation evolution equation, and the same applies to the flux of potential enthalpy.

The intuitive explanation of why Conservative Temperature makes sense

These lectures have largely demonstrated the benefits of potential enthalpy and Conservative Temperature from the viewpoint of conservation equations, but the benefits can also be deduced by the following parcel-based argument.

1. First, the air-sea heat flux needs to be recognized as a flux of potential enthalpy which is exactly c_p^0 times the flux of Conservative Temperature.
2. Second, the non-conservative production of Conservative Temperature at non-zero pressure is calculated from the mixture of two seawater parcels (as in the non-equilibrium, Taylor series analysis of Eqn. (A.18.2)) and shown to be much less than that for potential temperature.
3. Third, note that the ocean circulation can be regarded as a series of adiabatic and isohaline movements during which Θ is absolutely unchanged (because of its "potential" nature) followed by a series of turbulent mixing events during which Θ is almost totally conserved.

Hence it is clear that Θ is the quantity that is advected and diffused in an almost conservative fashion and whose surface flux is exactly proportional to the air-sea heat flux.

The correct explanation of the adiabatic lapse rate Γ

The adiabatic lapse rate Γ is the change in *in situ* temperature t with pressure when entropy η and Absolute Salinity S_A are held constant. This vertical gradient of *in situ* temperature is commonly observed in the ocean in well-mixed layers, for example, the surface mixed layer, the benthic (bottom) mixed layer and occasionally at mid depth (e.g. in Meddies).

From the Fundamental Thermodynamic Relation Eqn. (A.7.1)

$$\boxed{du + (p + P_0)dv = dh - v dP = (T_0 + t)d\eta + \mu dS_A} \quad (\text{A.7.1})$$

we find that

$$\left. \frac{\partial h}{\partial \eta} \right|_{S_A, p} = \hat{h}_\eta = (T_0 + t) \quad \text{and} \quad \left. \frac{\partial h}{\partial P} \right|_{S_A, \eta} = \hat{h}_p = v, \quad (\text{Laspse_1a,b})$$

where we consider enthalpy in the functional form $h = \hat{h}(S_A, \eta, p)$. Now differentiate Eqn. (Lapse_1a) with respect to pressure, to find that

$$\begin{aligned} \Gamma &= \left. \frac{\partial t}{\partial P} \right|_{S_A, \eta} = \left. \frac{\partial t}{\partial P} \right|_{S_A, \Theta} = \left. \frac{\partial^2 h}{\partial \eta \partial P} \right|_{S_A} = \hat{h}_{\eta p} = \left. \frac{\partial v}{\partial \eta} \right|_{S_A, p} = \frac{v_T}{\eta_T} \Big|_{S_A, p} = \frac{v_\Theta}{\eta_\Theta} \Big|_{S_A, p} = \frac{v_\Theta}{\eta_\Theta} \Big|_{S_A, p} \\ &= -\frac{g_{TP}}{g_{TT}} = -\frac{\eta_p}{\eta_T} = \frac{(T_0 + t)\alpha^t}{\rho c_p(S_A, t, p)} \\ &= \frac{\tilde{v}_\Theta}{\tilde{\eta}_\Theta} = \frac{(T_0 + \theta)\alpha^\theta}{\rho c_p(S_A, \theta, 0)} \\ &= \frac{\hat{v}_\Theta}{\hat{\eta}_\Theta} = \frac{(T_0 + \theta)}{c_p^0} \hat{v}_\Theta = \frac{(T_0 + \theta)}{c_p^0} \hat{h}_{p\Theta} = \frac{(T_0 + \theta)\alpha^\theta}{\rho c_p^0}. \end{aligned} \quad (2.22.1)$$

The reference pressure of the potential temperature θ that appears in the last two lines of Eqn. (2.22.1) is $p_r = 0$ dbar. Here the thermal expansion coefficients are

$$\begin{aligned}\alpha^t &= -\left.\frac{1}{\rho} \frac{\partial \rho}{\partial T}\right|_{S_A, p} = \left.\frac{1}{v} \frac{\partial v}{\partial T}\right|_{S_A, p} = \frac{g_{TP}}{g_P} \\ \alpha^\theta &= -\left.\frac{1}{\rho} \frac{\partial \rho}{\partial \theta}\right|_{S_A, p} = \left.\frac{1}{v} \frac{\partial v}{\partial \theta}\right|_{S_A, p} = \frac{g_{TP}}{g_P} \frac{g_{TT}(S_A, \theta, 0)}{g_{TT}} \quad (\text{thermal_expansion}) \\ \alpha^\Theta &= -\left.\frac{1}{\rho} \frac{\partial \rho}{\partial \Theta}\right|_{S_A, p} = \left.\frac{1}{v} \frac{\partial v}{\partial \Theta}\right|_{S_A, p} = -\frac{g_{TP}}{g_P} \frac{c_p^0}{(T_0 + \theta) g_{TT}}.\end{aligned}$$

The adiabatic (and isohaline) lapse rate Γ is commonly (and incorrectly) explained as being proportional to the $(p+P_0)dv$ work done on a fluid parcel as its volume changes in response to a change of pressure. According to this explanation the adiabatic lapse rate Γ would increase linearly with (i) pressure and (ii) the fluid's compressibility, but neither of these dependencies occur.

This incorrect explanation starts with the Fundamental Thermodynamic Relation in the form

$$du + (p+P_0)dv = (T_0+t)d\eta + \mu dS_A, \quad (\text{A.7.1})$$

and for an isentropic and isohaline change in pressure the right-hand side is zero. An increase in pressure in this isentropic and isohaline situation means that the change in specific volume v is given in terms of the isentropic and isohaline compressibility $\kappa = -v^{-1}v_P|_{S_A, \eta}$ as $dv = -v\kappa dP$ and the change in internal energy is

$$du = (p+P_0)v\kappa dP = v\kappa d\left(\frac{1}{2}[p+P_0]^2\right). \quad (\text{Lapse}_1)$$

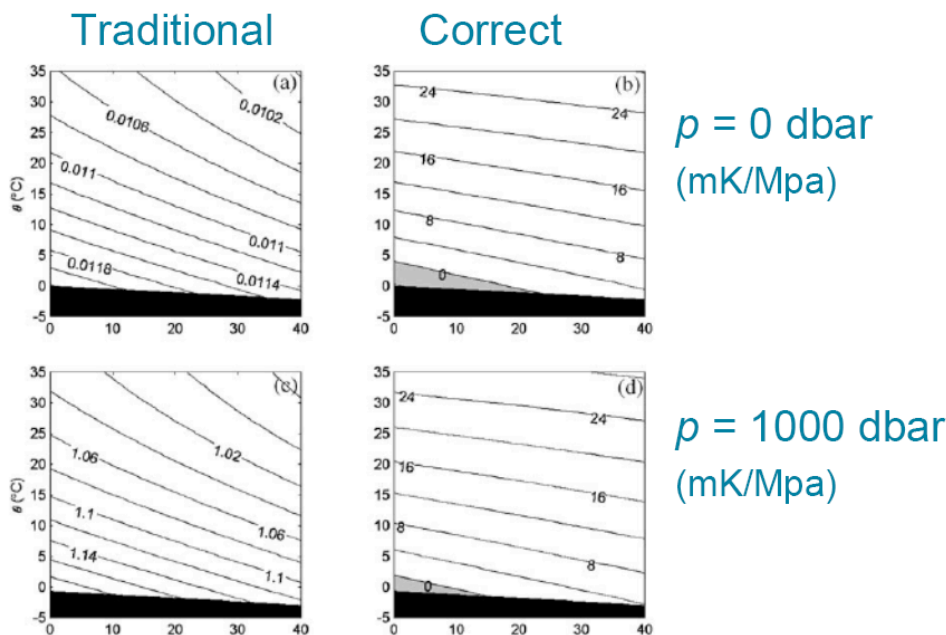
So far this is correct; an isentropic and isohaline increase in pressure does indeed increase the parcel's internal energy u by exactly this amount.

Then the traditional (and incorrect) explanation says that this increase in internal energy u results in a corresponding increase in *in situ* temperature, by dividing du by an appropriate specific heat capacity. This step is incorrect because the dependence of internal energy on pressure has been ignored. That is, regarding $u = u(S_A, t, p)$, the total derivative of internal energy is

$$du = u_{S_A} dS_A + u_T dT + u_P dP, \quad (\text{Lapse}_2)$$

and the traditional explanation of the adiabatic lapse rate assumes that the last term here is zero. While this is true of a perfect gas, it is very "untrue" of a liquid like water and seawater. For a liquid this term can be two or three orders of magnitude larger than $du = (p+P_0)v\kappa dP$, so the dominant balance in Eqn. (Lapse_2) for a liquid is $0 \approx u_T dT + u_P dP$.

What causes the adiabatic lapse rate?



The adiabatic lapse rate is (a) proportional to the thermal expansion coefficient and (b) is independent of the fluid’s compressibility. Indeed, the adiabatic lapse rate changes sign at the temperature of maximum density (where α^t, α^θ and α^θ all change sign) whereas the compressibility is always positive. This change in sign of the adiabatic lapse rate Γ occurs even though the work done by compression, $(p + P_0)dv$, is always positive (for a increase in pressure).

Hence, in cold lakes where the thermal expansion coefficient is negative, the adiabatic lapse rate is negative, so that as the pressure is increased adiabatically, the *in situ* temperature actually decreases! The adiabatic lapse rate Γ represents that change in temperature that is required to keep the entropy (and also θ and Θ) of a seawater parcel constant when its pressure is changed in an adiabatic and isohaline manner.

The traditional explanation has found its way into our textbooks because it works perfectly for a perfect gas; the missing term that we identified just happens to be zero for a perfect gas, but it is the dominant term for a liquid.

Remember, the adiabatic lapse rate has nothing whatsoever to do with the $(p + P_0)dv$ work done in changing the internal energy of a fluid parcel. This explanation is wrong even for a perfect gas (where you get the right answer for the wrong reason); for a liquid it is wrong by orders of magnitude.

The adiabatic lapse rate and the potential temperature of ice Ih

Ice Ih is the form of ice with hexagonal packing of the water molecules. This is the form of ice that is found in the range of temperatures and pressures found on planet earth.

The adiabatic lapse rate is equal to the change of *in situ* temperature experienced when pressure is changed while keeping entropy (and salinity) constant. This definition applies separately to both ice and seawater (where one needs to keep not only entropy but also Absolute Salinity constant during the pressure change). In terms of the Gibbs functions of seawater and of ice Ih the adiabatic lapse rates of seawater Γ and of ice Γ^{lh} are expressed respectively as

$$\Gamma = \left. \frac{\partial t}{\partial P} \right|_{S_A, \eta} = \left. \frac{\partial t}{\partial P} \right|_{S_A, \Theta} = \left. \frac{\partial t}{\partial P} \right|_{S_A, \theta} = - \frac{g_{TP}}{g_{TT}} = \frac{(T_0 + t) \alpha^t}{\rho c_p}, \quad (\text{Ice}_1)$$

and

$$\Gamma^{\text{lh}} = \left. \frac{\partial t}{\partial P} \right|_{\eta} = \left. \frac{\partial t}{\partial P} \right|_{\theta^{\text{lh}}} = - \frac{g_{TP}^{\text{lh}}}{g_{TT}^{\text{lh}}} = \frac{(T_0 + t^{\text{lh}}) \alpha^{\text{lh}}}{\rho^{\text{lh}} c_p^{\text{lh}}}, \quad (\text{Ice}_2)$$

where α^t and α^{lh} are the thermal expansion coefficients of seawater and ice Ih respectively with respect to *in situ* temperature.

The adiabatic lapse rates of seawater and of ice are numerically substantially different from each other. The thermal expansion coefficient of ice does not change sign as does that of seawater when it is cooler than the temperature of maximum density, and the specific heat capacity of ice c_p^{lh} is only approximately 52% that of seawater c_p .

Figure Ice_1(a) below shows the ratio $\Gamma/\Gamma^{\text{lh}}$ of the adiabatic lapse rates of seawater and ice at the freezing temperature, as a function of the Absolute Salinity of seawater and pressure. For salinities typical of the open ocean, the ratio $\Gamma/\Gamma^{\text{lh}}$ is about 0.1 indicating that the *in situ* temperature of ice varies ten times as strongly with pressure when both seawater and ice Ih are subjected to the same isentropic pressure variations. This must be taken into account when considering the vertical motion of frazil ice and the vertical motion of seawater and frazil ice mixtures.

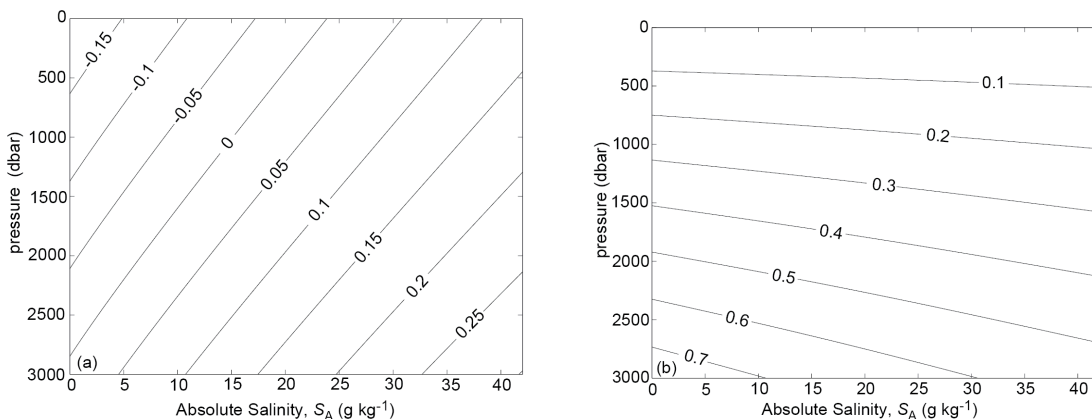


Figure Ice_1. (a) The ratio of the adiabatic lapse rates of seawater and of ice Ih, $\Gamma/\Gamma^{\text{lh}}$, at the freezing temperature. (b) The difference (in $^{\circ}\text{C}$) between the potential temperatures of seawater θ and of ice θ^{lh} for parcels of seawater and ice whose *in situ* temperature is the *in situ* freezing temperature.